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Effect of Hydrocarbon Composition on Oxidant-Hydrocarbon Relationships. Phase II Blend of Total Hydrocarbon Emissions

Exxon Research & Engineering Co., Linden, N.J.

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To assess the formation of atmospheric oxidants resulting from exhaust emitted by catalyst-equpped vehicles,chamber irradiations were conducted using a hydrocarbon blend representing total hydrocarbon emissions (exhaust, refueling and evaporation). Results were compared with previous irradiation results using a hydrocarbon blend representing non-methane, non-acetylene exhaust emissions from non-catalyst vehicles or catalyst-equipped vehicles. The blend representing total hydrocarbon emissions produced significantly less oxidants than either of the other two blends.

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EFFECT OF HYDROCARBON COMPOSITION ON OXIDANT-HYDROCARBON RELATIONSHIPS

Phase II. Blend of Total Hydrocarbon Emissions

by

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ABSTRACT

Phase I of this contract effort explored the effect of the change in auto exhaust hydrocarbon composition due to the installation of catalytic exhaust control on automobiles on the formation of atmospheric oxidant. In Phase I, 28 experimental and 2 comparison smog chamber irradiations were performed under static, dilution, and dynamic flow conditions. Fourteen of these runs used a hydrocarbon mixture representative of the non-methane, non-acetylene exhaust hydrocarbon emissions from a non-catalyst equipped car, and 14 used a hydrocarbon mixture representative of the same fraction of the emissions from a car equipped with an oxidation catalyst. The production of oxidant and other parameters of the reaction were followed, and the data was analyzed for significant changes in oxidant formation with hydrocarbon composition.

In Phase II, a third hydrocarbon blend modeled on the total hydrocarbon emissions (exhaust, refueling, and evaporative) from a catalyst-equipped vehicle was run under the conditions used in Phase I. The results of these runs were compared against the Phase I results in terms of significant effects on photochemical smog formation.

In the Phase II tests, the blend based on total vehicle hydrocarbon emissions produced significantly less severe photochemical smog manifestations than either of the other two blends. The clear stratification of the blends in terms of maximum 1-hour average ozone production and the apparent linear decrease of maximum 1-hour average ozone with increasing paraffin mole fraction indicate that the concept of hydrocarbon reactivity is applicable to smog chamber data taken with long irradiations (10-hour $\sim$ 2 solar days) and under a variety of simulated meteorological conditions, including ventilation with clean and polluted air. Of the three reactivity scales tested, all underestimated the reactivity differences between the blends. However, the oldest scale developed by Altshuller in 1966 fits the data better than two recently proposed scales. Further work is necessary to determine whether a scale capable of accurately predicting over a wide range of conditions and blend compositions can be developed.

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SECTION 1

INTRODUCTION

As control of the hydrocarbon (HC) emissions from automobile exhaust becomes increasingly strict, other sources of hydrocarbon loss connected with vehicle operation become increasingly important. Recent work at Exxon Research allows the estimation of losses from two of these sources: (1) evaporation from the fuel system, and (2) refueling emissions.

Evaporative losses occur during normal diurnal thermal cycling of the vehicle fuel system and during changes in the fuel system temperature due to vehicle operation. These losses have been subject to control since 1971 at a level of 2 g HC/test, with a test simulating one day's operation. Using 10,000 mi/year/ vehicle, evaporative losses from vehicles meeting this standard amount to ∿0.07 g/mi.*

Refueling losses occur when liquid is pumped into a vehicle fuel tank, displacing hydrocarbon vapors into the atmosphere. Control of such losses has been proposed for the major metropolitan areas. Exxon Research has measured refueling losses for an uncontrolled vehicle using a laboratory simulation and found them to range from 2 g/gal. to 5 g/gal. of fuel dispensed, depending on temperature and fuel vapor pressure. Under typical late summer conditions, emissions are ∿0.24 g/mi. at a projected 1980 fuel economy of 17 mpg. We have also obtained detailed compositional data for hydrocarbon emissions from this source.

The sum of losses from these two sources, 0.31 g/gal., is 75% of the 1978 exhaust hydrocarbon emission standards. Given the magnitude of this contribution to total vehicle emissions, these losses should certainly be taken into account when assessing the impact of controls on the oxidant-forming potential of vehicle hydrocarbon emissions. This report covers smog chamber studies of a hydrocarbon blend modeled on the total emissions from a vehicle which meets the strict (0.41 g/mi.) exhaust emission standards using an oxidation catalyst.

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*Due to the nature of the measurements in this report, the English System of Units was used. For conversion to the International System of Units, see the conversion table on p. 18.

SECTION 2

CONCLUSIONS

The data from this work indicate that the oxidant-forming potential of the composite hydrocarbon mix, including exhaust, evaporative, and refueling emissions, is less than that of the exhaust emissions alone. It is, therefore, important to consider all three sources of hydrocarbons when assessing the impact of motor vehicle operations on oxidant air quality. For example, the effect of transportation controls on a region would be overestimated if the total quantity of hydrocarbons removed were considered to have the oxidant-forming potential of exhaust.

It also appears that the concept of hydrocarbon reactivity is applicable to the prediction of oxidant levels during long term (10-hour) irradiations under a variety of simulated meteorological conditions. This finding, with irradiations approximately equivalent to 2 solar days of real world exposure and runs including ventilation of the system with both clean and polluted air, indicates that a valid reactivity scale for use under transport conditions is feasible. Of three reactivity scales tested, all underestimated the reactivity differences between the blends. The scale proposed by Altshuller in 1966 did, however, give a better fit to the data than two more recently proposed scales. Further work is necessary to determine if a scale capable of accurately predicting over a wide range of conditions and blend compositions can be developed.

In evaluating the implications of the above results, the uncertainties involved in extrapolating smog chamber data to the real world should be noted. In general, only trends, not absolute results, should be applied to actual atmospheric situations.

SECTION 3

EXPERIMENTAL PLAN

The oxidant-forming potential of a hydrocarbon blend modeled on the total emissions from a vehicle which meets the strict exhaust emission standards (0.41 g/mi) was studied in the Exxon Research Environmental Chamber. Ten-hour irradiations were carried out under three different initial hydrocarbon-to-NO_x ratios and three different modes of chamber operation, as given in the matrix below:

	Initial HC/NO_x ($\frac{ppmC}{ppm}$)		
Chamber Operating Mode	2	4	8
static	X	X	X
dilution		X	X
dynamic		X	X

Initial hydrocarbon concentration levels were 4 ppm carbon for HC/NO_x ratios of 4 and 8, and 2 ppm carbon for an HC/NO_x ratio of 2. Initial nitrogen oxides (NO_x) consisted of 30% nitrogen dioxide (NO_2) and 70% nitric oxide (NO).

Time/concentration profiles for ozone (O_3), NO, NO_2, peroxyacetylnitrate (PAN), total hydrocarbons, condensation nuclei, and individual hydrocarbons were determined. Oxidant was determined by the Neutral Buffered Potassium Iodide (NBKI) method and formaldehyde was determined by the chromatropic acid method at the beginning and end of the run only. This experimental design is identical to that used in Phase I of this contract effort. It allows direct comparison of the oxidant-forming potential of this blend to that of the catalyst and non-catalyst exhaust blends tested in Phase I. The analysis and discussion in Phase II have focused on such comparisons.

SECTION 4

METHODS AND PROCEDURES

EQUIPMENT

Experimental work was carried out using the Exxon Research Environmental Chamber facility. A description of the chamber and associated analytical methodology follows.

The Environmental Chamber

The 4.25 m^3 Exxon Research Environmental Chamber is made of an aluminum frame with windows of Teflon film. The chamber resembles a flattened elliptical cylinder with cross-sectional dimensions of 2.75 m x 1.83 m and length of 0.99 m. The chamber surface is calculated to be 16.1 m^2, about 50% of which is associated with the two Teflon windows, resulting in a surface-to-volume ratio of 3.78 m^{-1}. The chamber is equipped with a metered purified air supply and metered vents which allow it to be run in dynamic modes.

Irradiation System

The irradiation system, designed to simulate ambient sunlight both in light intensity and spectral distribution of energy, consists of 80 fluorescent lamps, a combination of black and sun lamps. The light intensity in the chamber was determined by an Eppley Laboratories Model TUVR Solar Ultraviolet Radiometer (290-380 nm) to be approximately 48 mcal min^{-1} cm^{-2}.

Air Supply

An air purification system, consisting of a charcoal absorption tower and a platinum oxidation catalyst, provides pure air with less than 0.3 ppmC hydrocarbon. The hydrocarbon was analyzed and found to be solely methane. A measure of chamber background reactivity is obtained by irradiating this clean air in the chamber with humidity for 10 hours. The maximum number of condensation nuclei (CN) monitored was 182 CN/ml, which is three orders of magnitude lower than that observed with irradiated auto exhaust diluted to atmospheric levels. No increase in HC concentration was observed over the period of irradiation. Oxidant levels reached a maximum of 0.015 ppm.

CHAMBER OPERATING CHARACTERISTICS

Leak Rate and Sampling Requirements

To ensure that the chamber contents will not be contaminated by atmospheric air, the chamber pressure is maintained at 0.13 kPa above atmospheric

pressure. This results in an unintentional leak rate of less than 1.5% $hr.^{-1}$, which is measured by monitoring the amount of makeup air added. This volume is replaced with the purified air previously described. With the analytical procedures currently employed, the total leak rate of the chamber is about 3% $hr.^{-1}$. This volume is dependent upon the number and type of analytical measurements taken.

Relative Humidity and Temperature

The chamber is usually operated at approximately 30°C, the temperature being maintained by the use of infrared lamps. Temperature stability is adequate with a standard deviation of about 0.5°C over a 10-hour irradiation. Initial chamber humidity can be varied by circulating the diluent chamber air through a tank containing heated distilled water. The water temperature in the tank is maintained at about 80°C to reduce the time required for humidification.

Cleanliness

To ensure charber cleanliness and avoid run-to-run contamination, the chamber is purged with pure air containing about 2 ppm ozone between experiments. This has proven to be an effective means of maintaining chamber cleanliness.

It is believed that the rate of ozone disappearance in a chamber is a measure of chamber cleanliness. Ozone disappearance rates in air at 20% relative humidity were measured with and without irradiation. These rates, expressed as the half-life for O_3 at 1 ppm, are shown below. The values compare favorably with those of other chambers.

With irradiation, $t_{1/2}$ = 2.7 hours @ 20% R.H.

Dark reaction, $t_{1/2}$ = 14 hours @ 20% R.H.

ANALYTICAL METHODOLOGY

Total Hydrocarbons

Total hydrocarbons were measured with a Varian 1440 total hydrocarbon analyzer with a sensitivity of ~10 ppbC. The analyzer was zeroed on the chamber clean air supply and spanned on a commercially analyzed cylinder of propane (0.5 ppm) in air.

Individual Hydrocarbons

Individual hydrocarbons were measured with a Perkin Elmer Model 900 Gas Chromatograph with sub-ambient temperature programming capabilities. The instrument was equipped with a column 1/8" O.D., 5% UCW 98 on 80/100 mesh Chromosorb G AWDMCS. Fifty milliter samples were injected at -70°C and the column oven temperature was raised at a rate of 8°C/min. to 180°C. The instrument is calibrated on the initial chamber hydrocarbon charge, which is a metered dilution of a commercially analyzed cylinder.

Nitrogen Oxides

Nitrogen oxides were monitored with a TECO 14B nitrogen oxides analyzer. The analyzer is calibrated on a commercially analyzed cylinder using a TECO Model 101 calibration unit.

Oxidants

Oxidants were determined by the Neutral Buffered Potassium Iodide Procedure according to the Federal Reference Method (Fed. Reg. Vol. 36, #84, p. 8196), and corrected for NO_2 by subtracting 0.1 (NO_2).

Ozone

Ozone was measured with a REM Chemiluminescent Analyzer calibrated on the ozone generator in the TECO 101 calibration unit. The ozone generator is calibrated by Neutral Buffered Potassium Iodide according to the Federal Reference Method.

Peroxyacetylnitrate

Peroxyacetylnitrate determinations were carried out with a Varian Model 1700 gas chromatograph with electron capture detector. Calibration is by dilution of PAN mixtures synthesized in-house. Concentration of these mixtures is determined by long path infrared spectroscopy.

Formaldehyde

Formaldehyde concentrations were determined by the chromatropic acid method (U.S. Dept. HEW, 999-AP-11).

Condensation Nuclei

Condensation nuclei were monitored with an Environment One Condensation Nuclei Monitor, which operates on the cloud chamber principle.

REAGENTS AND CALIBRATION GASES

All reagents and calibration gases were obtained as analyzed cylinders from Scott Research Laboratories in Plumsteadville, Pennsylvania and used without further purification.

Nitrogen Oxides

Separate cylinders of NO_2 (~1000 ppm in hydrocarbon-free nitrogen) and NO (~1000 ppm in hydrocarbon-free nitrogen) were used to charge NO_x for all runs.

Hydrocarbon Blend

The hydrocarbon blend used in this study was derived from gas chromatographic data taken at Exxon Research and Engineering Co. The catalyst exhaust data was the same as that used to derive the catalyst blend for Phase

I. Refueling emissions were as measured from 9 lb. Reid Vapor Pressure (RVP) fuel dispensed at a temperature of 80°F into a fuel tank containing the same fuel at 90°F. Emissions from this particular run were 4.26 g/gal. of dispensed fuel. It was assumed that evaporative losses had the same composition as refueling losses. The composition of the final blend was constructed by summing the mole fractions of paraffins, olefins, and aromatics from exhaust with 3/4 of their counterparts from refueling and dividing the total by 1.75. Isopentene, the most common olefin in the refueling losses, was chosen as typical of olefin losses from that source. C_2/C_3 olefin and C_7/C_8 aromatic ratios were taken from the exhaust data. Methane and acetylene from exhaust were not considered, as they are photochemically unreactive. Table 1 gives the composition of the hydrocarbon blend used and compares parameters calculated from this blend with the same parameters from the chromatographic data.

PROCEDURE

After an overnight flush with clean air, the chamber was pressurized to 0.13 kPa above atmospheric pressure and checked for background ozone, oxidant, hydrocarbon, and NO_x. If these values were essentially zero, chamber humidity was set and the chamber was charged to the initial reactant levels in the following order:

1) NO_2 (to 30% of total NO_x)

2) NO (balance of total NO_x)

3) hydrocarbon

Initial readings of all instruments were taken after charging and before turning on the lights. Instruments were read at half-hour intervals for the first 5 hours of each run and at hourly intervals for the second 5 hours. Oxidant and formaldehyde were determined only at the end of the run after the lights had been shut off. Three different modes of chamber operation were used:

- Static - Only air necessary to make up for sampling losses was added. Results were corrected for this small dilution before reporting. Initial relative humidity was set at 12%.**
- Dilution - The chamber was operated statically for the first 5 hours of irradiation and then diluted at a rate of 10%/hour with purified air. This mode was intended to simulate a temperature inversion which holds throughout the morning and then breaks up. Results were not corrected for dilution. Initial relative humidity was set at 20%.

**Due to an arithmetical error, average relative humidity was not held constant over all running modes, so effects due to change in running modes may be, in part, due to differences in relative humidity.

TABLE 1. PHASE II HYDROCARBON BLEND AND CALCULATED PARAMETERS

COMPOSITION OF HYDROCARBON BLEND

Compound	Mole Fraction
ethylene	0.10
propylene	0.02
n-butane	0.67
isopentene	0.07
toluene	0.08
xylene	0.06

CALCULATED PARAMETERS

Parameter	Target Value (Chromatographic data)	Blend Value
mole fraction paraffins	0.65	0.67
mole fraction olefins	0.20	0.19
mole fraction aromatics	0.15	0.14
average paraffin carbon #	4.50	4.0
average olefin carbon #	3.75	3.2
average aromatic carbon #	7.30	7.4
C_2/C_3 olefin ratio	4.7	5.0
C_7/C_8 aromatic ratio	1.62	1.33

- Dynamic - The chamber charge was diluted at a rate of 10%/hour from the beginning of the run with purified air and reactants at a concentration of 0.4 ppmC hydrocarbon and 0.1 ppm NO. This mode was intended to represent the transport of a polluted air mass across a populated area where it is diluted and simultaneously receives injections of reactants. Results were not corrected for dilution. Initial relative humidity was set at 70%.**

At the end of each run, the chamber was flushed for 8 hours with clean air, treated with ozone at ~2 ppm for 2 hours with the lights on, and flushed overnight with clean air. To facilitate the determination of statistically significant trends in the data, runs were performed in random order.

**Due to an arithmetical error, average relative humidity was not held constant over all running modes, so effects due to change in running modes may be, in part, due to differences in relative humidity.

SECTION 5

RESULTS AND DISCUSSION

DATA ORGANIZATION AND PRESENTATION

Raw data from each chamber run were punched on cards and fed into an IBM 1130 computer. The computer converted raw instrument readings into concentrations in ppm, corrected these concentrations for dilution as necessary, and output the results in graphical form. Smooth curves were drawn through the line printer plots from the computer and further parameters were calculated from these curves. The formulae used to calculate these parameters are listed in Appendix A. The computer output sheets are available from the Project Officer. Calculated parameters and graphs for all runs appear in Appendix B.

Runs at $HC/NO_x = 2$

Runs at this level showed no evidence of reaction. They were not analyzed further.

Runs at $HC/NO_x = 4$ and $HC/NO_x = 8$

Runs at these levels showed evidence of reaction in all chamber operating modes. All of the subsequent analyses and conclusions are based on these runs.

Condensation Nuclei Data

Condensation nuclei concentrations (CNC) were of the order of 10^2/ml for all runs. This extremely low absolute concentration level is near the limits of detectability for our CNC counter. It is believed that any variability in CNC readings is due to the noise inherent in operating the instrument at these low levels, so no detailed analysis of these data was carried out.

DATA ANALYSIS

The 12 runs with $HC/NO_x = 4$, and $HC/NO_x = 8$, chamber running conditions of static, dilution, and dynamic ,and non-catalyst and catalyst hydrocarbon blends form a completely replicated 3 x 2 factorial experimental design. One of the basic characteristics of this design is that factor effects, i.e., those due to HC/NO_x and chamber running conditions, are completely clear of all two-factor interaction effects, and the interaction effects are clear of each other. Replication allows the variance in the measurements to be estimated and the statistical significance of any observed effects to be determined.

TABLE 2. PARAMETERS ANALYZED

Ozone, maximum 1-hour average
Ozone, time to maximum
NO_2, maximum 1-hour average
NO_2, time to maximum
PAN, maximum
Oxidant, final
Formaldehyde, final
Total Hydrocarbon, average disappearance rate
Individual Hydrocarbons, average disappearance rate*

* Analyzed by simple analysis of variance for compound-to-compound differences as missing data did not allow a full factor analysis.

For these data, analysis of variance was carried out for the parameters in Table 2. (The analysis of variance tables are given in Appendix C.) This group includ all of the parameters necessary to make a good assessment of the effects of the factors in the experimental matrix on photochemical smog production. All of the single factor and two-way interaction effects significant at the 95% level were determined using the standard F test for comparison of the variance due to the factor and the variance determined from the replicate experiments. Significant blend effects were determined by comparing the mean parameter levels from this set of runs with the mean levels from the Phase I data. The Phase I blends were modeled after the non-acetylene, non-methane fraction of exhaust emissions from catalyst equipped and non-catalyst equipped automobiles. Table 3 gives the composition of these blends. The standard t test was used to determine whether differences due to changing blend were significant at the 95% level. All significant effects found in the present study and all significant blend effects are given below in RESULTS. (The 95% confidence intervals used in this test and plotted in the following figures are ∿2 times the standard deviation.)

It should be noted that very little significance can be attached to the absence of an effect in this analysis. The experimental design and variance of the measurements are such that the probability of not detecting an effect (the β risk) of .03 ppm in maximum ozone, maximum NO_2, or final oxidant is ∿50% when the test for that effect is carried out at the 95% significance level.

TABLE 3. PHASE I HYDROCARBON BLENDS

Compound	Mole Fraction	
	Non-Catalyst Equipped Car	Catalyst Equipped Car
n-pentane	0.21	—
n-butane	—	0.51
ethylene	0.30	0.18
propylene	0.09	0.04
toluene	0.17	0.17
m-xylene	0.23	0.10

RESULTS

Effect Due Only to Change in HC/NO_x Ratio

Changing the HC/NO_x ratio from 4 to 8 (or NO_x concentration from 1.0 ppm to 0.5 ppm):

- Decreased maximum 1-hour average NO_2 41%, from 0.41 ppm to 0.24 ppm, and
- Increased time to maximum NO_2 70%, from 1.0 to 1.7 hours.

It should be noted that in this set of experiments, HC concentration was held constant. Therefore, a change in HC ratio may equally be thought of as a change in total NO_x concentration.

Effects Due Only to Change in Chamber Running Mode

A change in chamber running conditions from static to dilution:

- Decreased time to maximum NO_2 50%, from 2.2 hours to 1.1 hours.

A change in chamber running conditions from static to dynamic:

- Decreased time to maximum ozone 55%, from 8.9 hours to 4.0 hours,
- Decreased time to maximum NO_2 64%, from 2.2 hours to 0.8 hours, and
- Increased average total hydrocarbon disappearance rate 280%, from 0.23 ppmC/hour to 0.87 ppmC/hour.

Effects due to Interactions Between HC/NO_x Ratio and Chamber Running Mode

Changing HC/NO_x ratio from 4 to 8 increased the time to NO_2 maximum 2.9 hours for static runs and did not change it significantly for dilution and dynamic runs.

Effects Due Only to Change in Hydrocarbon Blend

Changing hydrocarbon blend from one modeled on non-catalyst exhaust to one modeled on catalyst exhaust plus refueling losses plus evaporative emissions:

- Decreased maximum 1-hour average O_3 78%, from 0.23 ppm to 0.05 ppm,
- Increased time to maximum ozone 19%, from 5.4 hours to 6.4 hours,
- Decreased maximum 1-hour average NO_2 15%, from 0.39 ppm to 0.33 ppm,
- Decreased maximum PAN 87%, from 0.015 ppm to 0.002 ppm,
- Decreased final oxidant 67%, from 0.12 ppm to 0.04 ppm,
- Decreased final formaldehyde 42%, from 0.12 ppm to 0.07 ppm, and
- Decreased average total hydrocarbon disappearance rate 49%, from 0.88 ppmC/hour to 0.45 ppmC/hour.

Changing the hydrocarbon blend from one modeled on catalyst-treated

exhaust to one modeled on the same exhaust plus evaporative emissions plus refueling losses:

- Decreased maximum 1-hour average O_3 64%, from 0.14 ppm to 0.05 ppm, and
- Decreased final oxidant 56%, from 0.09 ppm to 0.04 ppm.

Individual Hydrocarbon Disappearance Rates for Static Runs

Of the six hydrocarbons studied, four (ethylene, toluene, xylene and propylene) did not differ significantly in disappearance rate. The average for this group was 0.009 ppm/hour. Isopentene disappeared significantly faster at 0.05 ppm/hr., while n-butane had a significantly slower rate of 0.002 ppm/hr.

Note on Dosages

Dosage calculations, being integrals under experimental curves, are highly dependent upon the time limits of the integration. Comparisons based on total dose are subject to an experimental artifact: if the effect of a change in experimental factor is to shift the O_3 or NO_2 maxima to a later time, and the dose integral is still cut off in 10 hours from the start of the run, the dose will be less, but it will be less only because the production was artificially terminated at the end of the run. Since the probability of missing a significant shift in time to maximum in this experiment is high (for a shift of 1 hour $p = 0.7$ for time to O_3 maximum), no effects on dose are reported as significant.

DISCUSSION

Examination of the statistically significant effects shows that the findings of this study can be easily summarized.

- The blend used in this study generally produced less severe manifestations of photochemical smog than the blends used in Phase I.
- Changing HC/NO_x ratio (or equivalently in this study, NO_x concentration) significantly effected only the maximum 1-hour average NO_2 concentration and the time to reach it.
- Changes in running mode produced significant effects only in times to maxima of O_3 and NO_2 and total hydrocarbon disappearance rate.

A clear ranking of the three blends in terms of the severity of photochemical smog produced under our reaction conditions can be deduced from the significant effect presented in Phase II and from the significant effects found in Phase I of this program. The Phase II blend clearly produces the least severe smog, exhibiting significant decrease from both other blends in maximum 1-hour average ozone and final (10-hour) oxidant, and significant decreases from the non-catalyst blend in maximum 1-hour average NO_2, maximum PAN, and 10-hour formaldehyde. The catalyst blend from Phase I is next in

severity, showing significant increases in maximum 1-hour average O_3 and final (10-hour) oxidant over the Phase II blend, but remaining significantly less (Phase I results) than the non-catalyst blend in maximum 1-hour average ozone and in maximum PAN. In addition, maxima in ozone occur significantly later in time for both the Phase II and catalyst blends as compared to the non-catalyst blend.

The data in this program do not allow analysis in terms of individual hydrocarbon reactivities as the three blends contain six hydrocarbons, which translates into a system of three equations and five unknowns. In fact, since the olefin and aromatic mole fractions are essentially equal within each of the blends, no good solution for reactivities on the basis of class can be found. It is clear, however, that ozone production drops off as mole fraction of paraffins increases and the drop-off is approximately linear over the range studied (Figure 1). This observation is interesting in that it indicates that the concept of hydrocarbon class reactivities might be applicable to data gathered in long term (10-hour) irradiation under a variety of simulated meteorological conditions, as well as to data from the more common 5-hour static irradiation runs.

Previously proposed reactivity scales were tested to see if they provided an adequate explanation for the difference in oxidant levels seen with these blends. Figure 2 shows a plot of measured vs. calculated relative ozone concentrations for the Phase I blends relative to the Phase II blend. Three different reactivity scales were used (1-3). All these scales underestimate the reactivity differences between the blends. The oldest scale, proposed by Altshuller in 1966, provided a better fit to the data than the two scales recently proposed by EPA and the California Air Resources Board. Additional work with blends in which class or compound effects can be clearly discerned is necessary to determine whether a scale capable of predicting over a wide range of blend compositions and running conditions can be developed.

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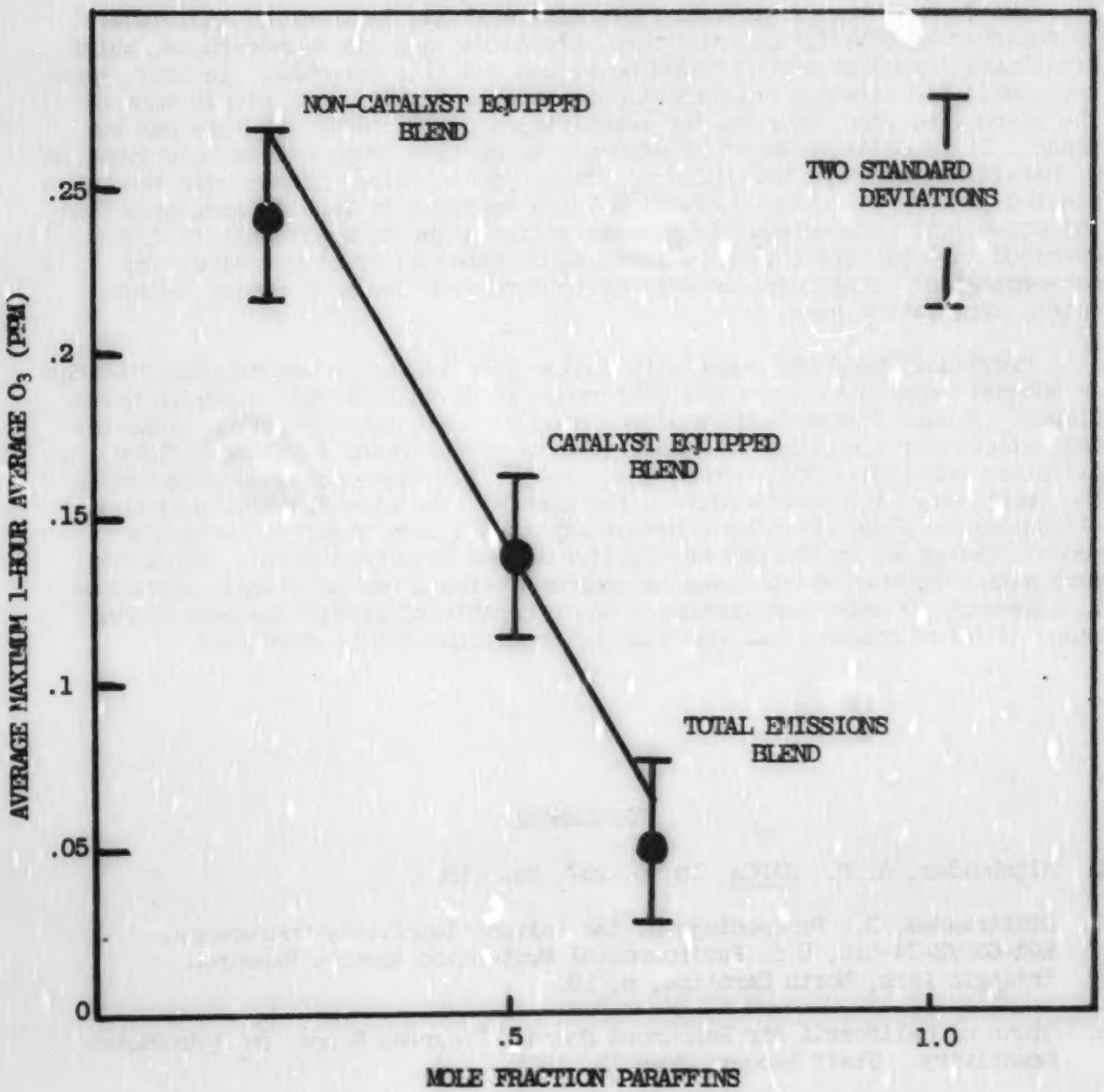

Figure 1. Average maximum 1-hour average ozone concentration vs. mole fraction of paraffins.

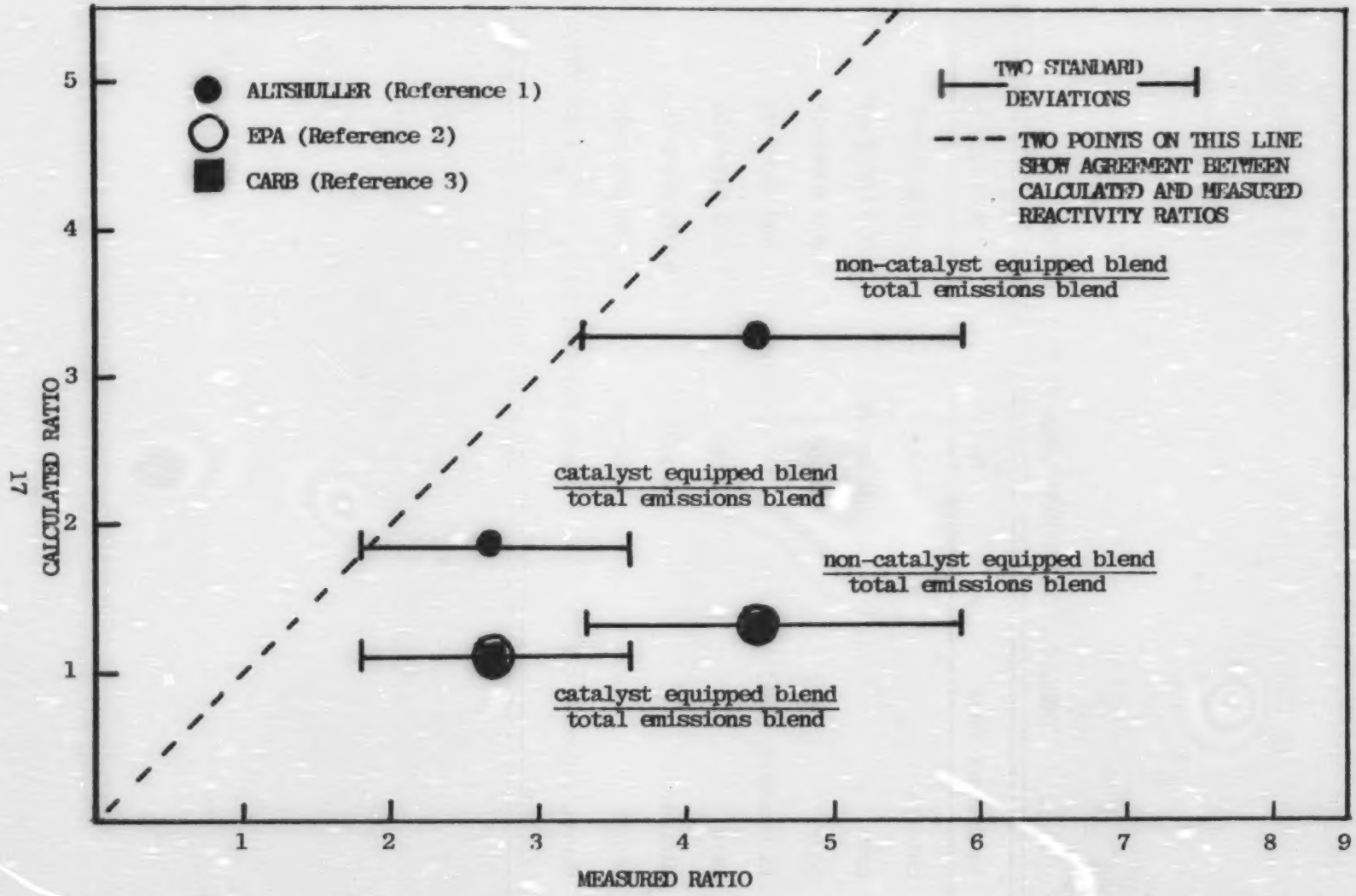

Figure 2. Calculated vs. measured ratio of average maximum 1-hour average ozone concentrations.

TABLE 4. CONVERSION TABLE TO S. I. UNITS

To Convert From	To	Multiply by
calorie	joule	4.186 8 E+00
gram	kilogram	1.000 000*E-03
hour	second	3.600 000*E+03
kilopascals (kPa)	newton/meter^2	1.000 000*E+03
mile	meter	1.609 344*E+03
minute	second	6.000 000*E+01
pound	kilogram	4.535 924 E-01
degree Fahrenheit (°F)	degree kelvin (°K)	$t_k = (t_F + 459.67)/1.8$

APPENDIX A

FORMULAE USED TO CALCULATE PARAMETERS

K_D = NO_2 photolysis rate constant

$$K_D = \frac{[NO]\,[O_3]}{[NO_2]}\ (29.5)\ min^{-1}\ *$$

where all concentrations are determined at the intersection point of the NO and O_3 curves.

$$NO_2\ Dose = \int_0^{10} [NO_2]\ dt\ ppm\ hrs.$$

$$O_3\ Dose = \int_0^{10} [O_3]\ dt\ ppm\ hrs.$$

**O_3 maximum 1-hour average =

$$\frac{O_3(max) + O_3(1/2\ hr.\ before\ max) + O_3(1/2\ hr.\ after\ max)}{3}$$

**NO_2 maximum 1-hour average =

$$\frac{NO_2(max) + NO_2(1/2\ hr.\ before\ max) + O_3(1/2\ hr.\ after\ max)}{3}$$

The project officer provided the following formulae:

$$NO_2\ formation\ rate = \frac{NO\ initial}{2T_{1/2}}\ ppm/hr.$$

where

$T_{1/2}$ = time at which NO_2 = 1/2 NO initial + NO_2 initial

$$Maximum\ rate\ of\ O_3\ formation = \frac{O_3(max)}{2\,(T_{3/4} - T_{1/4})}$$

---

* This formula is from: O'Brian, Environ. Sci. Tech., 8, 579, 1974.
**The formulae provide a good approximation to the true average for the broad maxima encountered in this work.

where

$T_{3/4}$ = time to form 3/4 of O_3 (max)

$T_{1/2}$ = time to form 1/4 of O_3 (max)

Average rate of O_3 formation = $\frac{O_3(max)}{2\ T_{1/2}}$

where

$T_{1/2}$ = time to form 1/2 of O_3 (max)

Maximum rate of hydrocarbon disappearance = $\frac{HC_i - HC_f}{2\ (T_{3/4} - T_{1/4})}$

where

HC_i = initial hydrocarbon concentration

HC_f = final hydrocarbon concentration

$T_{3/4}$ = time for disappearance of 3/4 (IHC_i - THC_f)

$T_{1/4}$ = time for disappearance of 1/4 (IHC_i - THC_f)

APPENDIX B

CALCULATED PARAMETERS AND GRAPHS

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RUN NO. 38: 2 ppm XL-263, 1 ppm NO_x, 0.3 ppm NO_2, STATIC
SEPTEMBER 2, 1975

Average Temperature = 32.95 ± 0.20 °C

Average Dilution Rate = $0.130 \times 10^{-1} \pm 0.122 \times 10^{-2}$ hr^{-1} chamber volumes

Concentrations are corrected for dilution

NO_2 Photolysis Rate Constant = Cannot calculate
No intersection of NO and O_3 curves

NO_2 Formation Rate = 0.06 ppm hr^{-1}

NO_2 Dose = 3.538 ppm hr

NO_2 is corrected for PAN

Maximum Rate of Ozone Formation = 0 ppm hr^{-1}

Average Rate of Ozone Formation = 0 ppm hr^{-1}

Ozone Dose = 0.001 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.08 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.13 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0 ppm

Initial Formaldehyde by Chromatropic Acid = 0 ppm

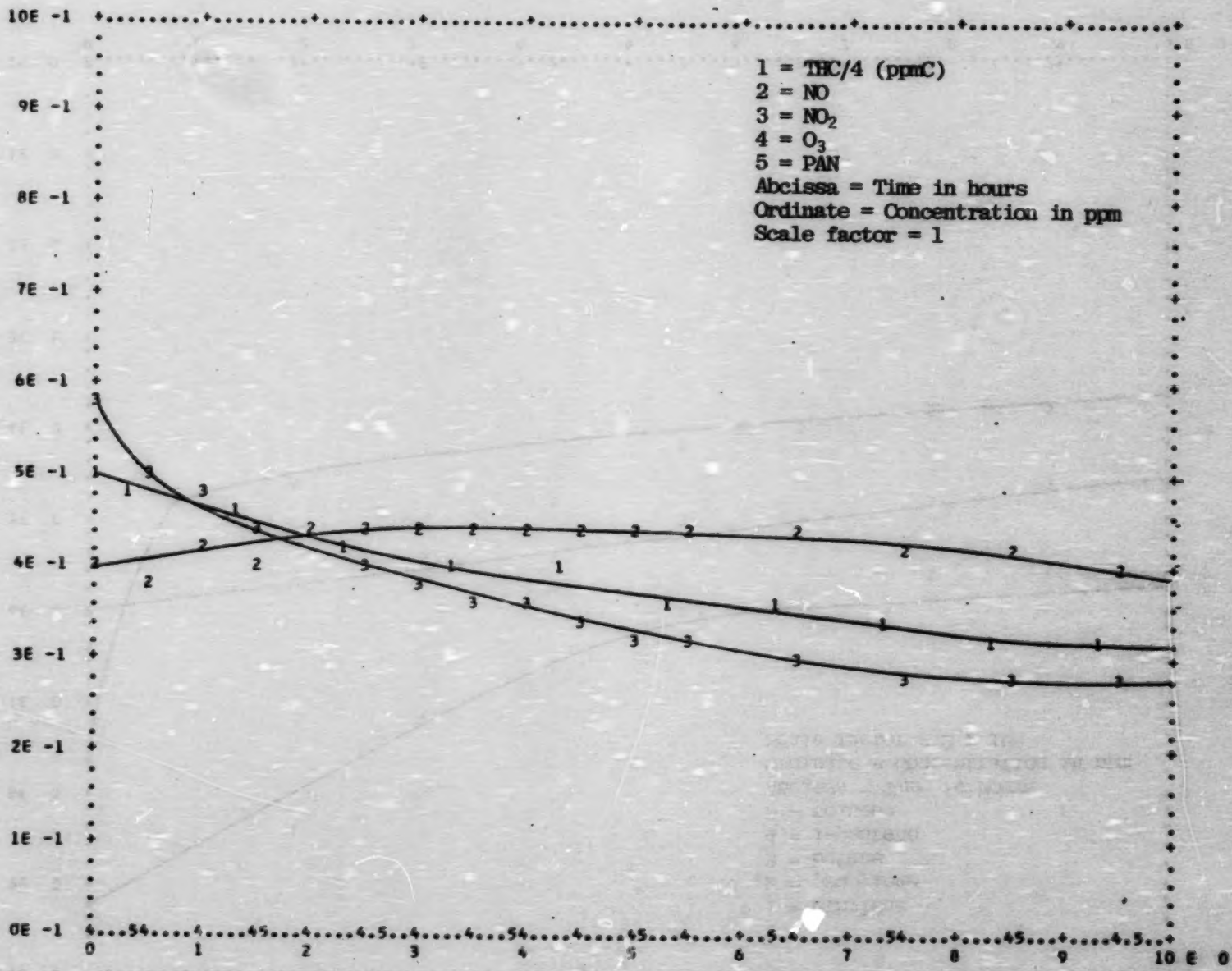
Final Formaldehyde by Chromatropic Acid = 0.05 ppm

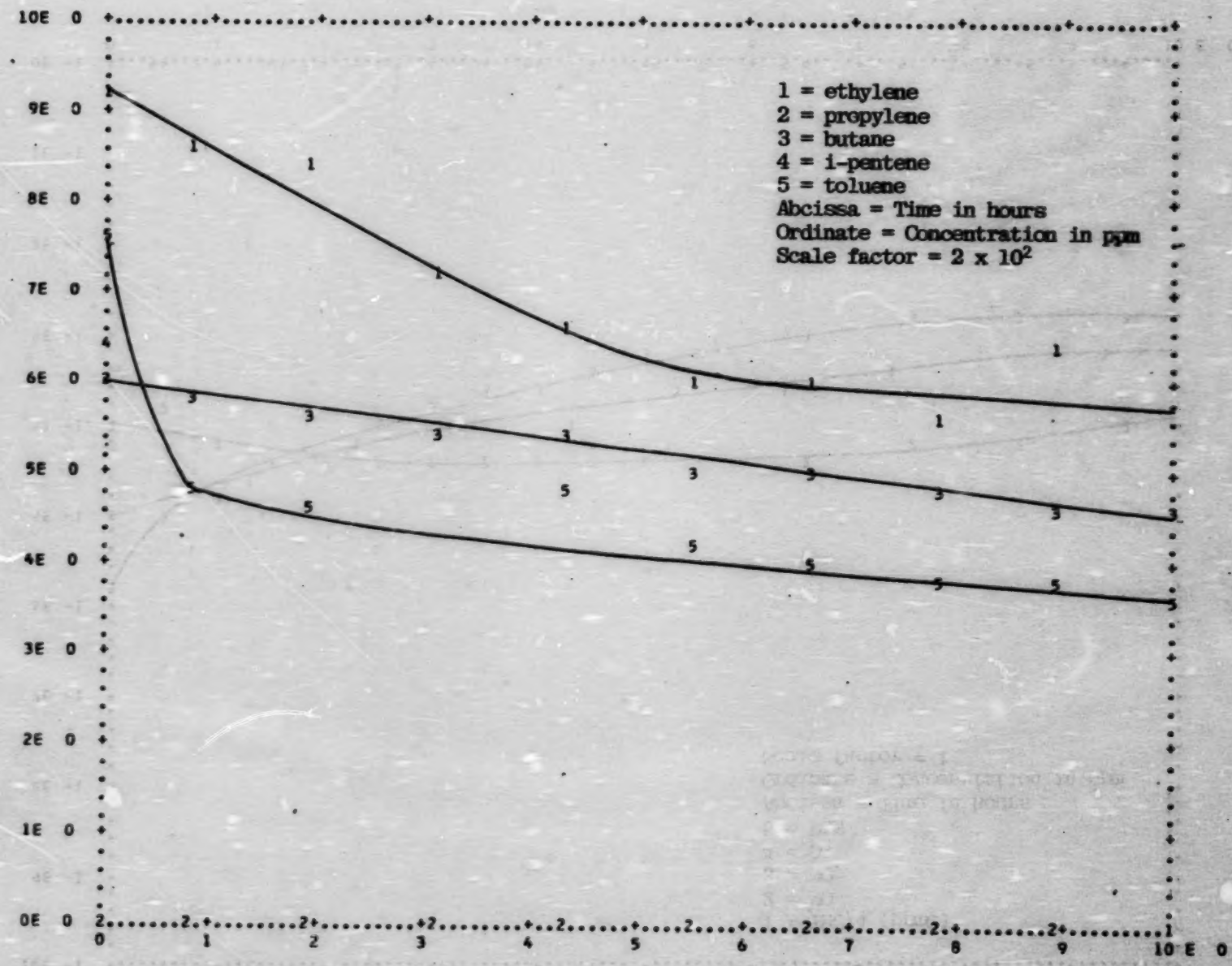
Maximum 1-hour O_3 Average = 0

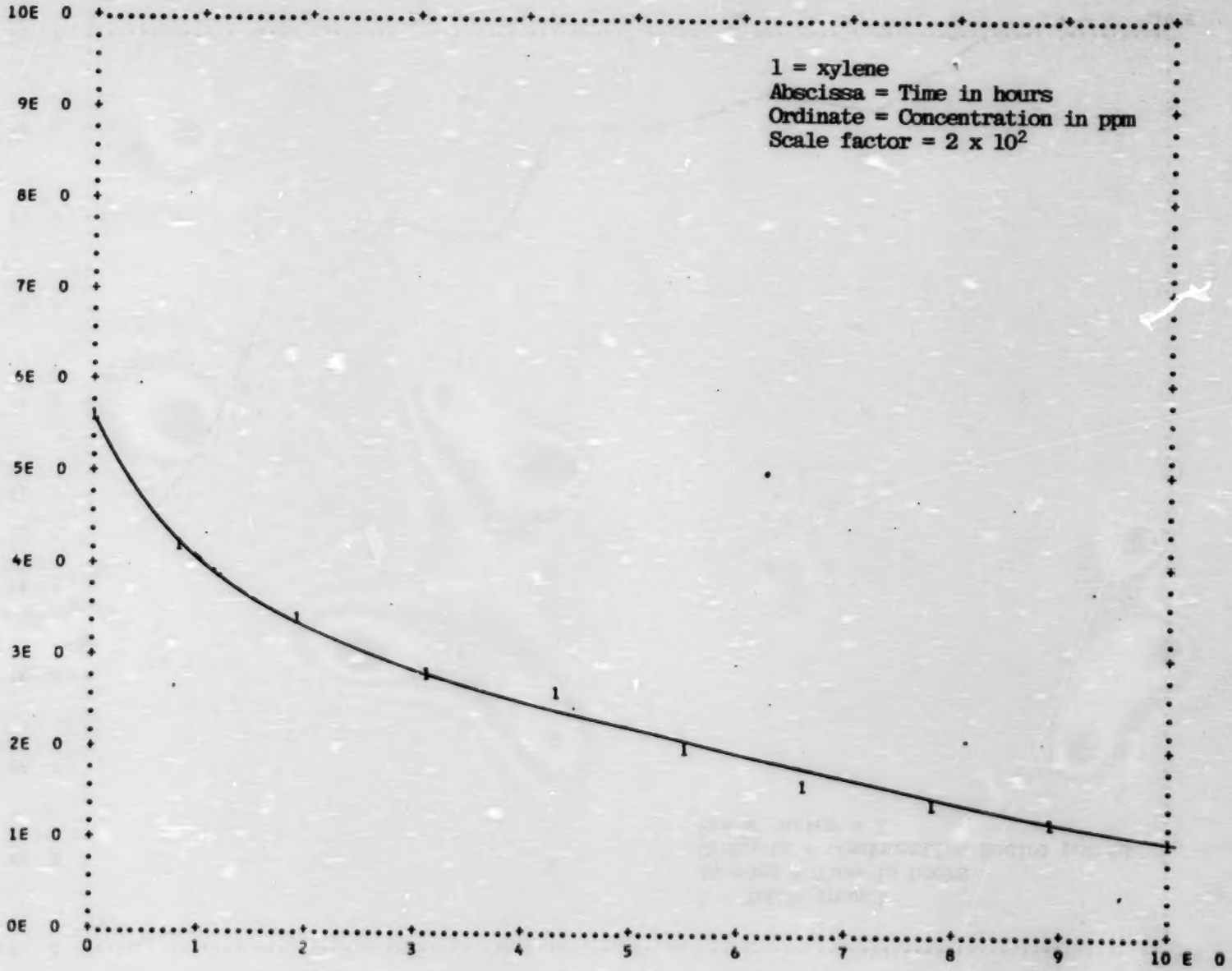
Maximum 1-hour NO_2 Average = 0.45

Average Hydrocarbon Disappearance Rate:

(1)	ethylene	= 0.0031
(2)	propylene	= 0
(3)	butane	= 0.0007
(4)	i-pentene	= 0
(5)	toluene	= 0.0222
(6)	xylene	= 0.0057


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0
1
2
3
4
5
6
7
8
9
10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 2 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abscissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 2 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
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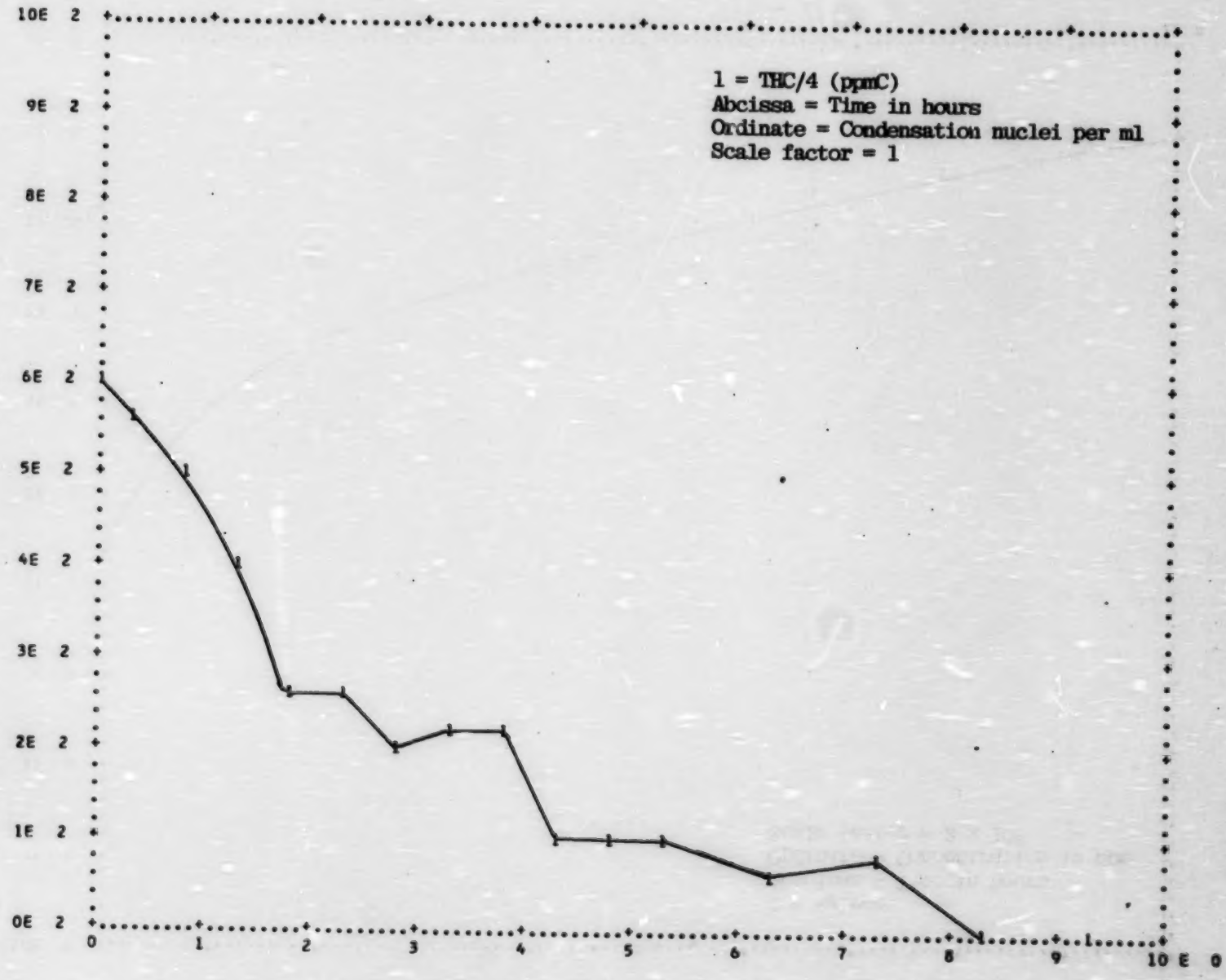
1
2
3
4
5
6
7
8
9
10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 1
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0
1
2
3
4
5
6
7
8
9
10 E 0

RUN NO. 35: 4 ppm XL-263, 1 ppm NO_x, 0.3 ppm NO_2, STATIC
AUGUST 20, 1975

Average Temperature = 33.02 ± 0.23 °C

Average Dilution Rate = $0.136 \times 10^{-1} \pm 0.861 \times 10^{-3}$ hr^{-1} chamber volumes

Concentrations are corrected for dilution

NO_2 Photolysis Rate Constant = 0.59 min^{-1}

NO_2 Formation Rate = 0.21 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 4.098 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0.02 ppm hr^{-1}

Average Rate of O_3 Formation = 0.01 ppm hr^{-1}

O_3 Dose = 0.509 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.20 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.29 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = <0.01 ppm

Final Oxidant by Neutral Buffered KI = 0.14 ppm

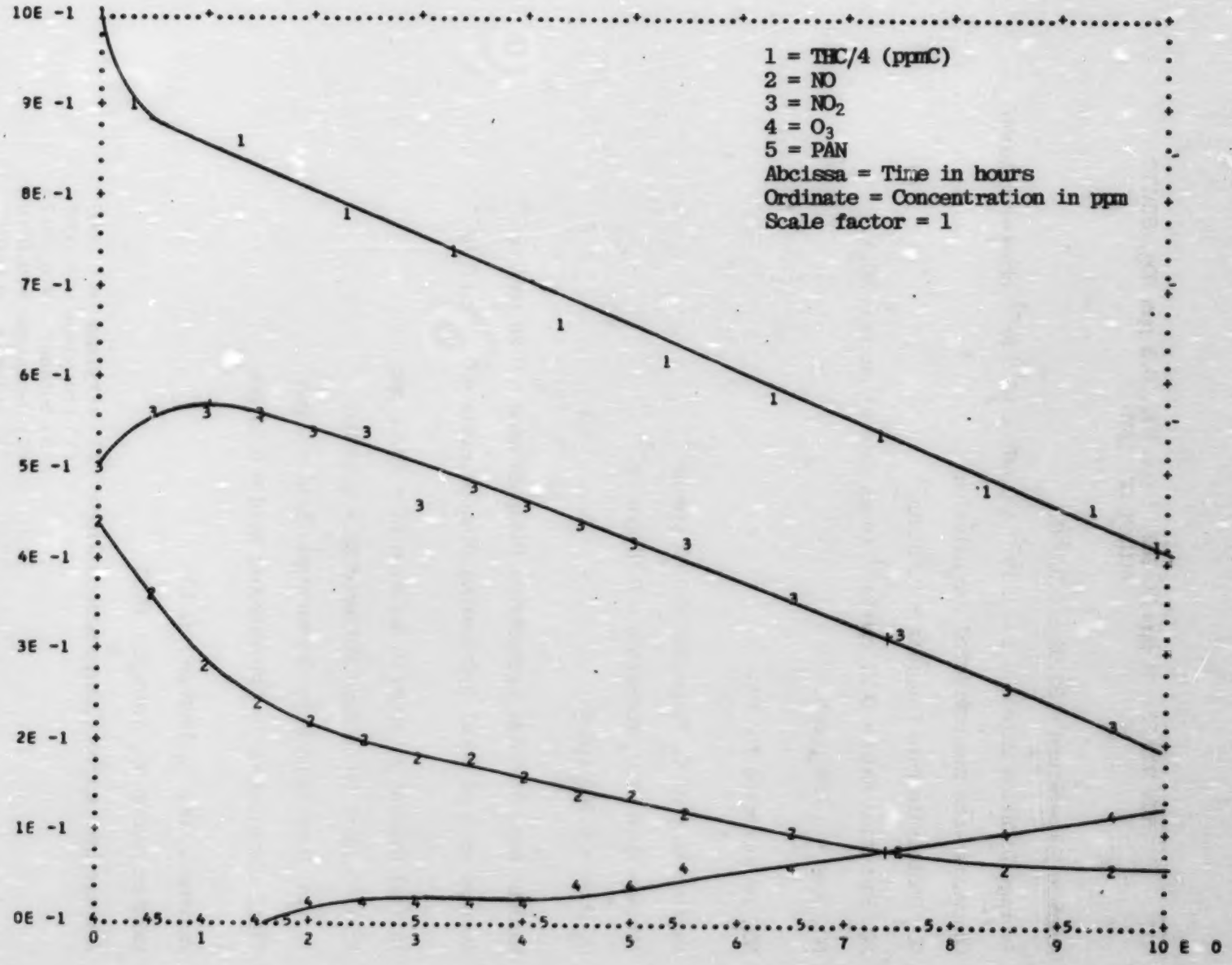
Initial Formaldehyde by Chromatropic Acid = 0 ppm

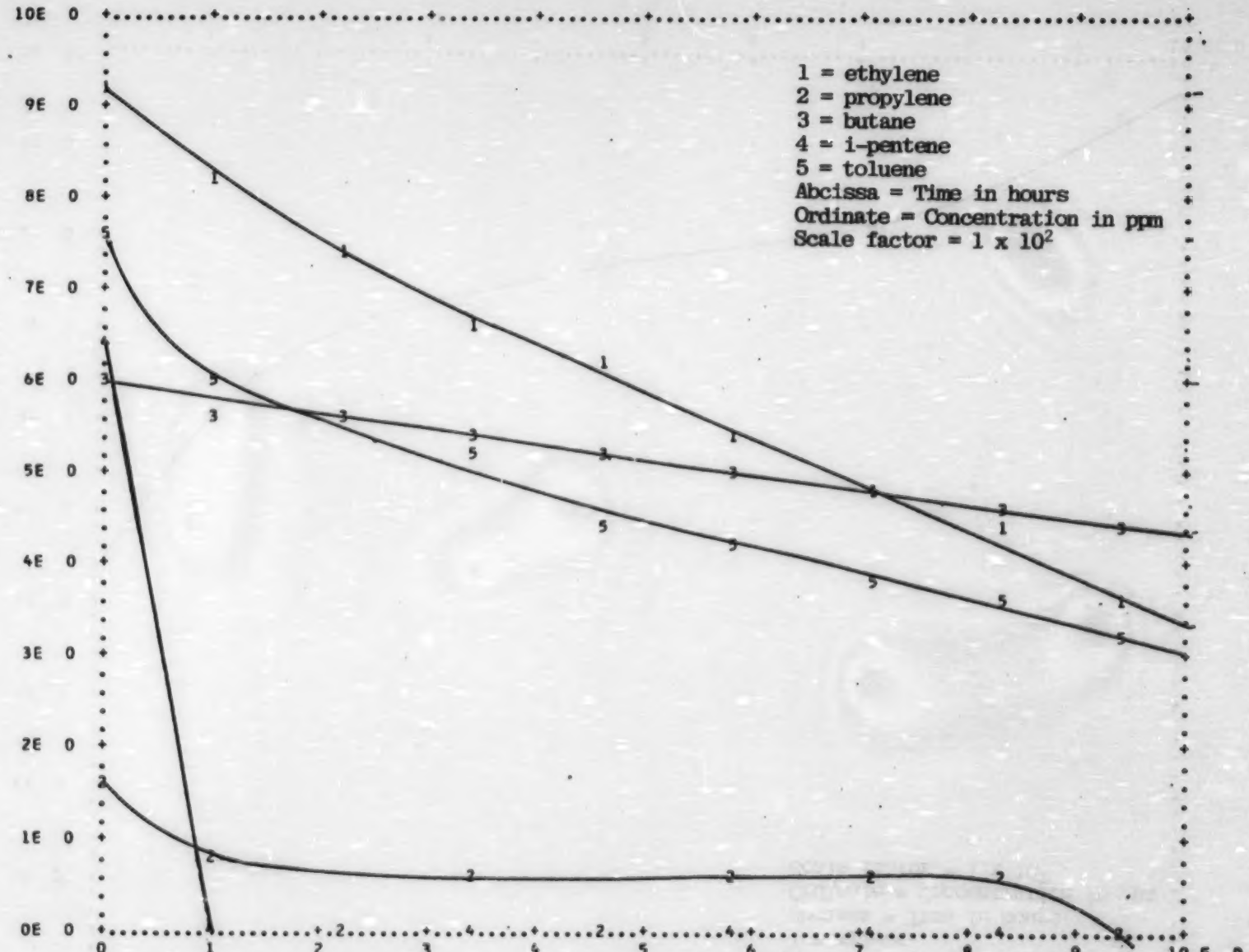
Final Formaldehyde by Chromatropic Acid = 0.26 ppm

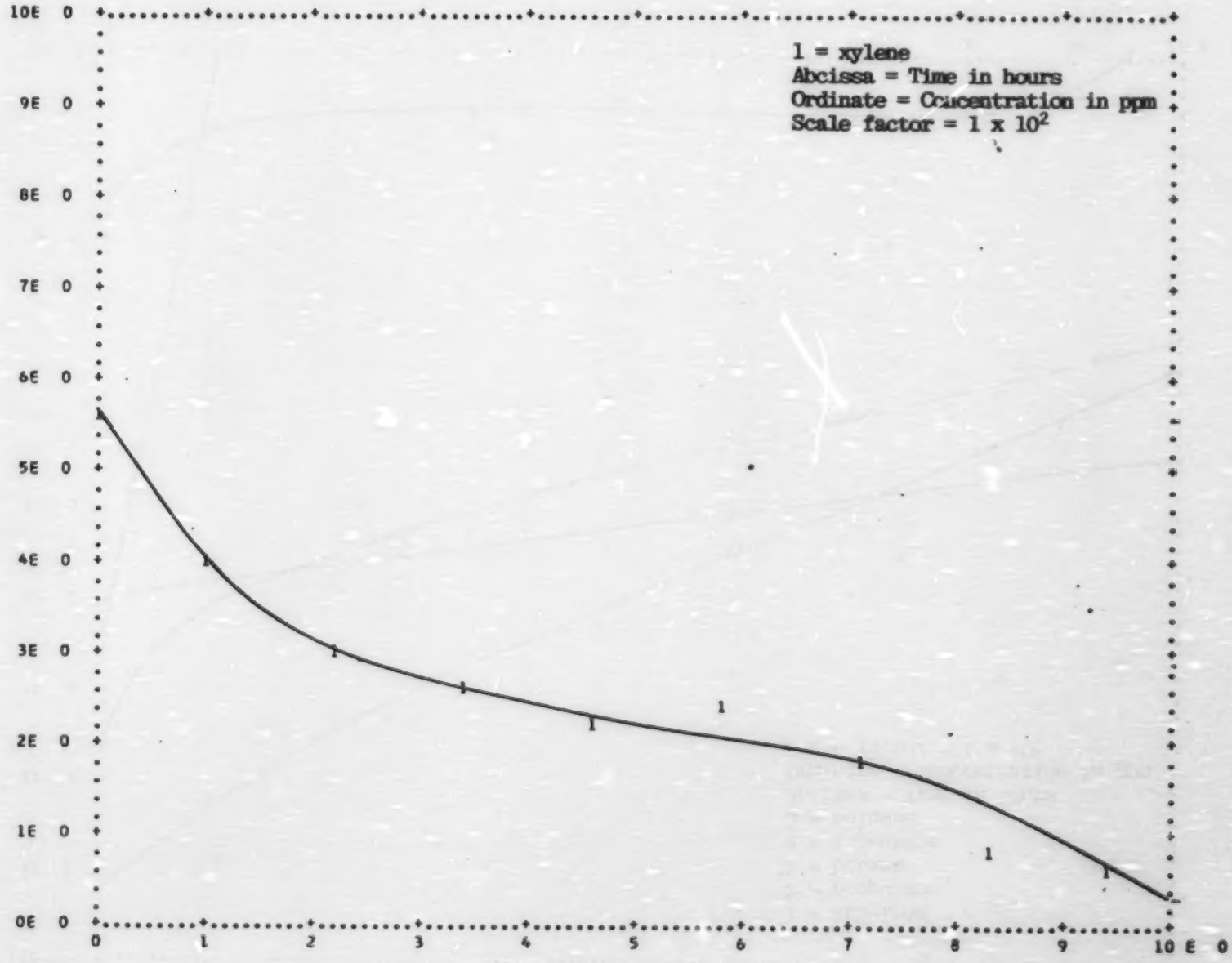
Maximum 1-hour O_3 Average = 0.13

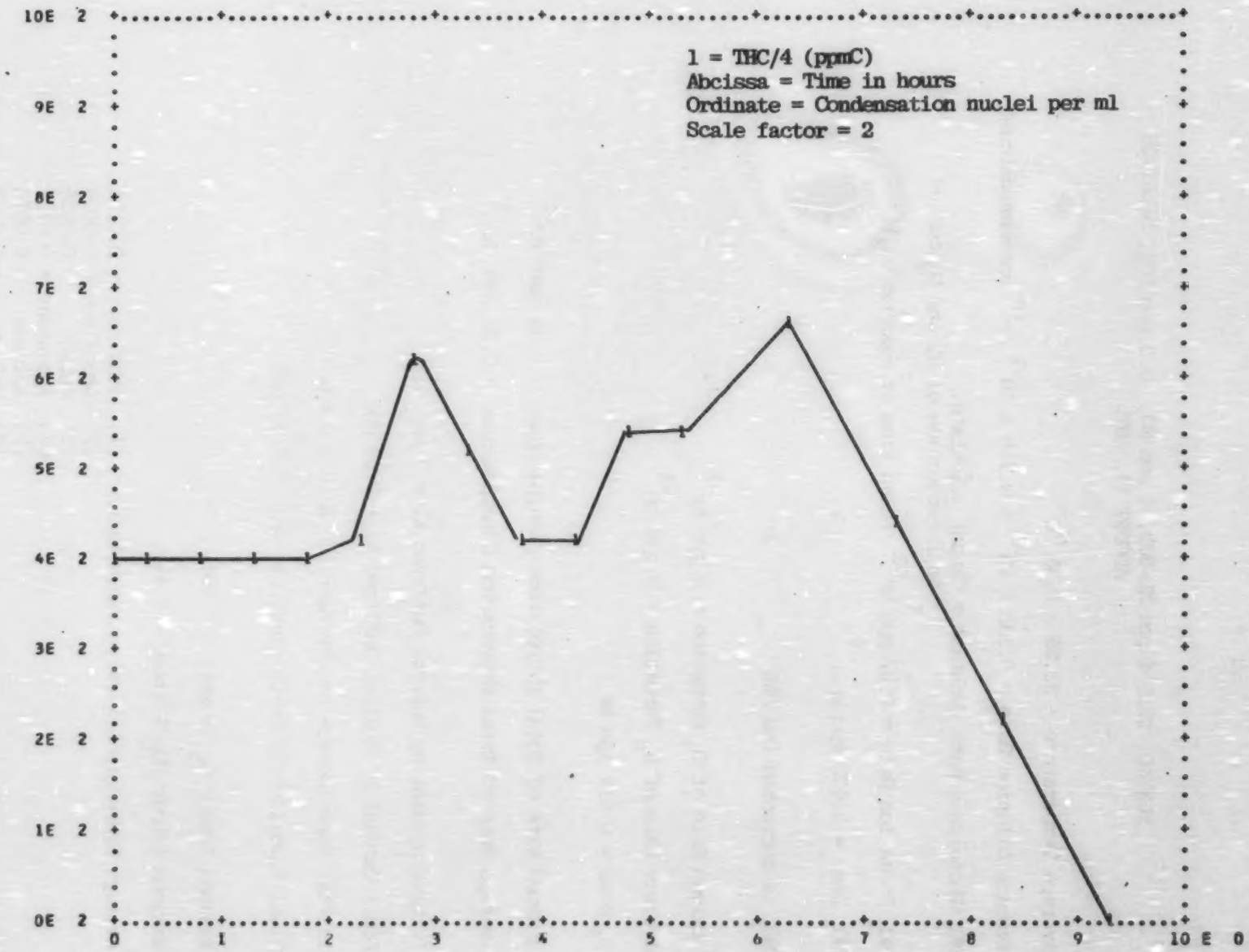
Maximum 1-hour NO_2 Average = 0.35

Average Hydrocarbon Disappearance Rates:
(1) ethylene = 0.0069
(2) propylene = 0.0094
(3) butane = 0.0017
(4) i-pentene = 0.0640
(5) toluene = 0.0092
(6) xylene = 0.0110


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10^2
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 2
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0
1
2
3
4
5
6
7
8
9
10 E 0

RUN NO. 33: 4 ppm XL-263, 1 ppm NO_x, 0.3 ppm NO_2, DILUTION
AUGUST 14, 1975

Average Temperature = 33.29 ± 0.33 °C

Average Dilution Rate = $0.583 \times 10^{-1} \pm 0.155 \times 10^{-1}$ hr^{-1} chamber volumes

NO_2 Photolysis Rate Constant = Cannot calculate.
No intersection of NO and O_3 curves.

NO_2 Formation Rate = 0.27 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 3.402 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0 ppm hr^{-1}

Average Rate of O_3 Formation = 0 ppm hr^{-1}

O_3 Dose = 0.018 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.32 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.24 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0.03 ppm

Initial Formaldehyde by Chromatropic Acid = 0 ppm

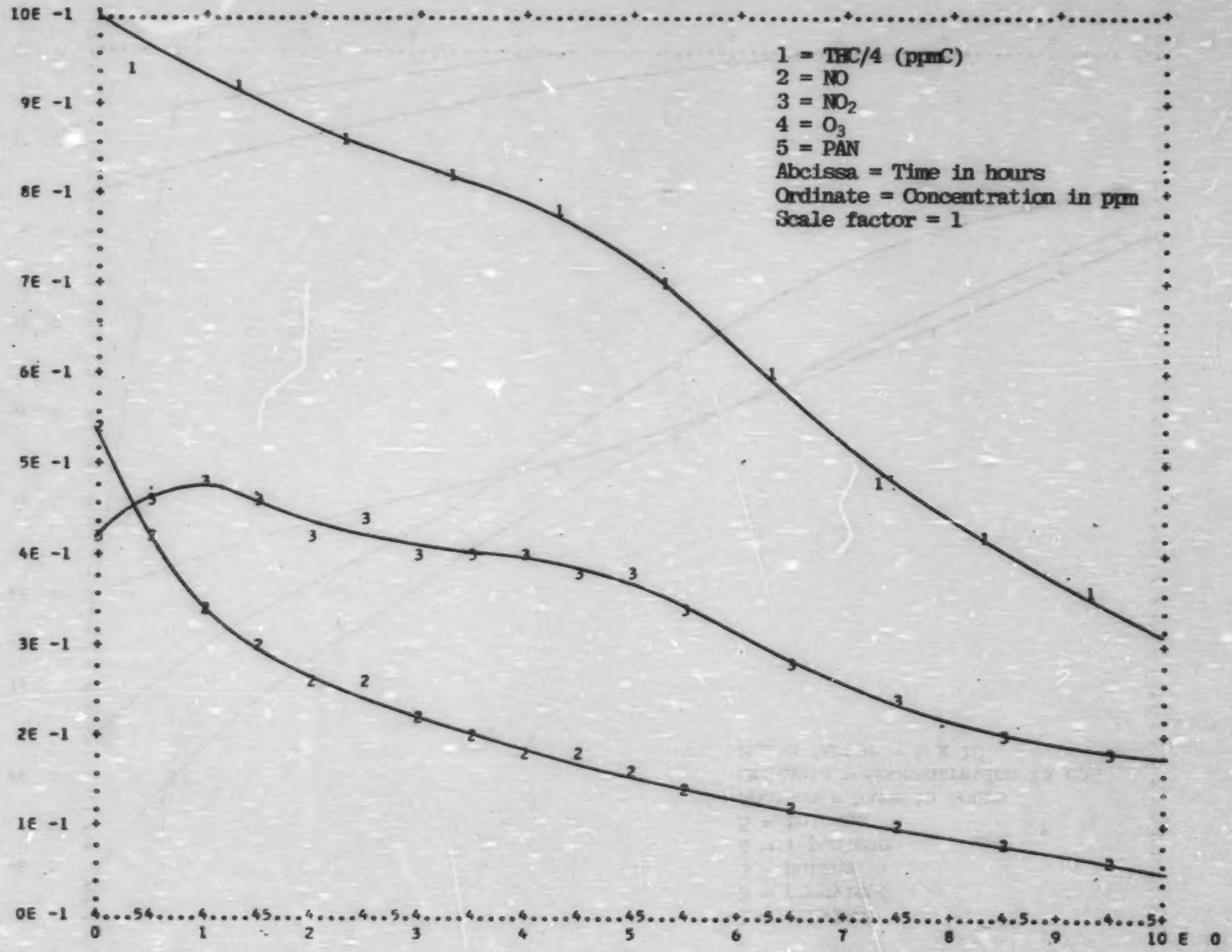
Final Formaldehyde by Chromatropic Acid = 0.07 ppm

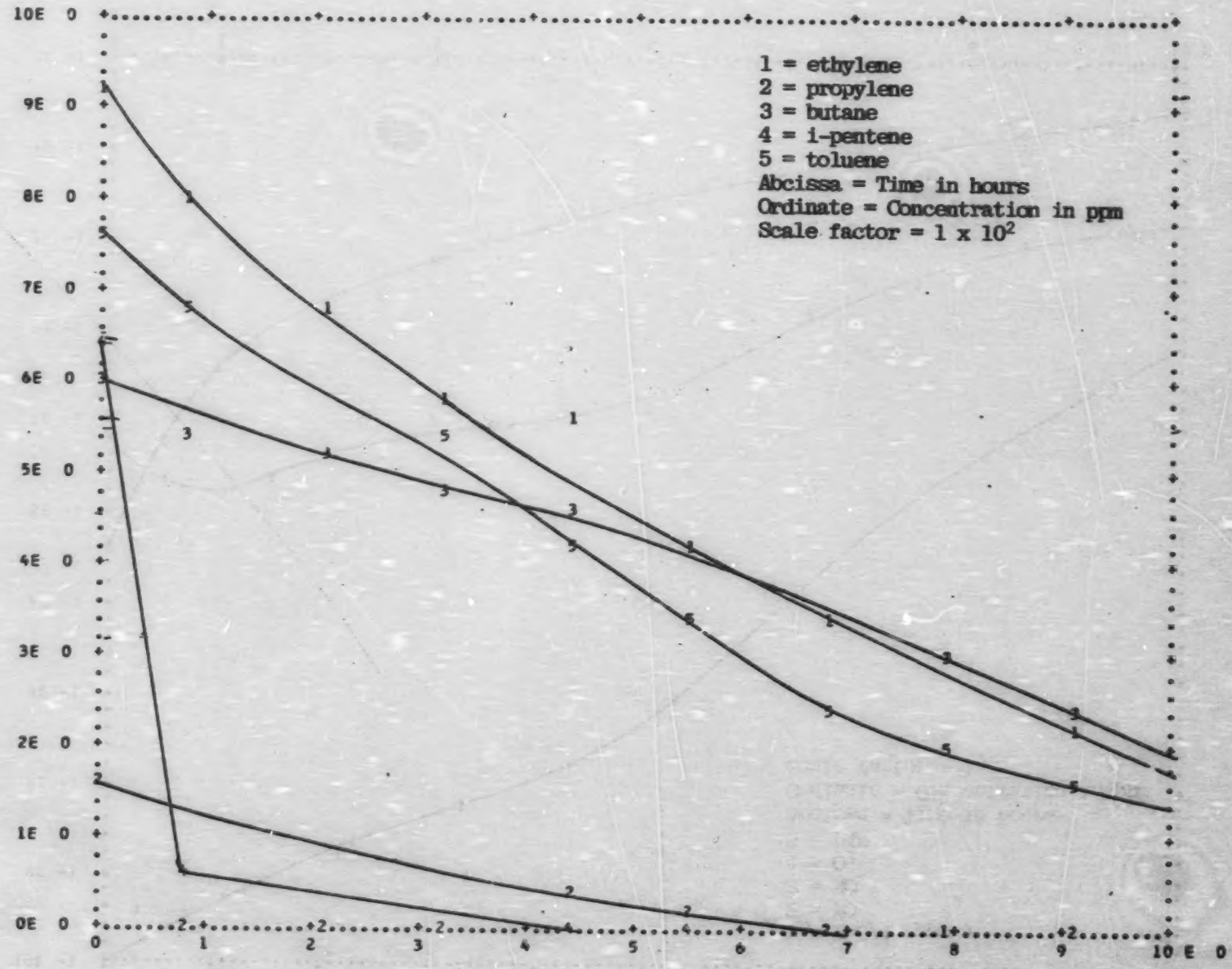
Maximum 1-hour O_3 Average = 0.004

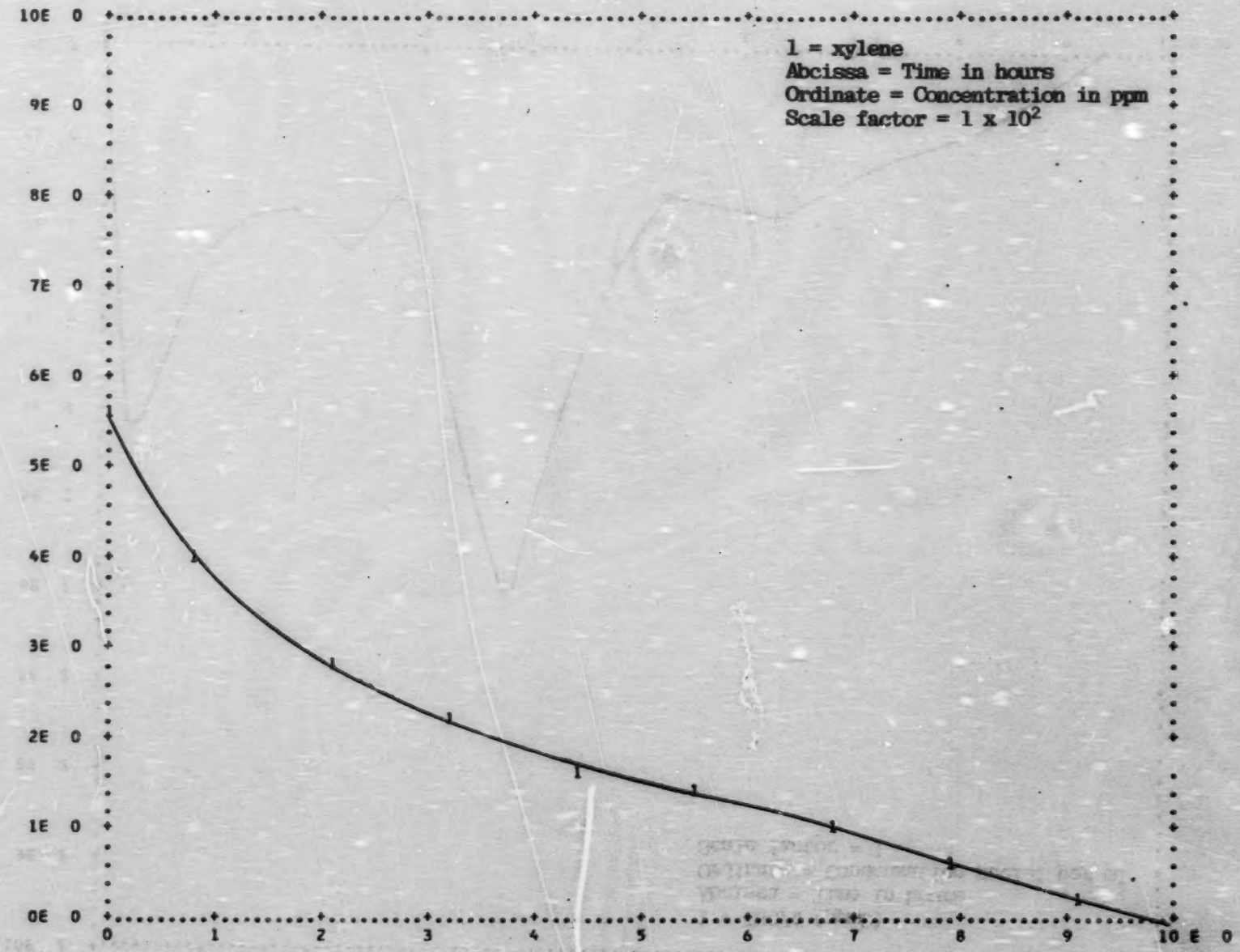
Maximum 1-hour NO_2 Average = 0.48

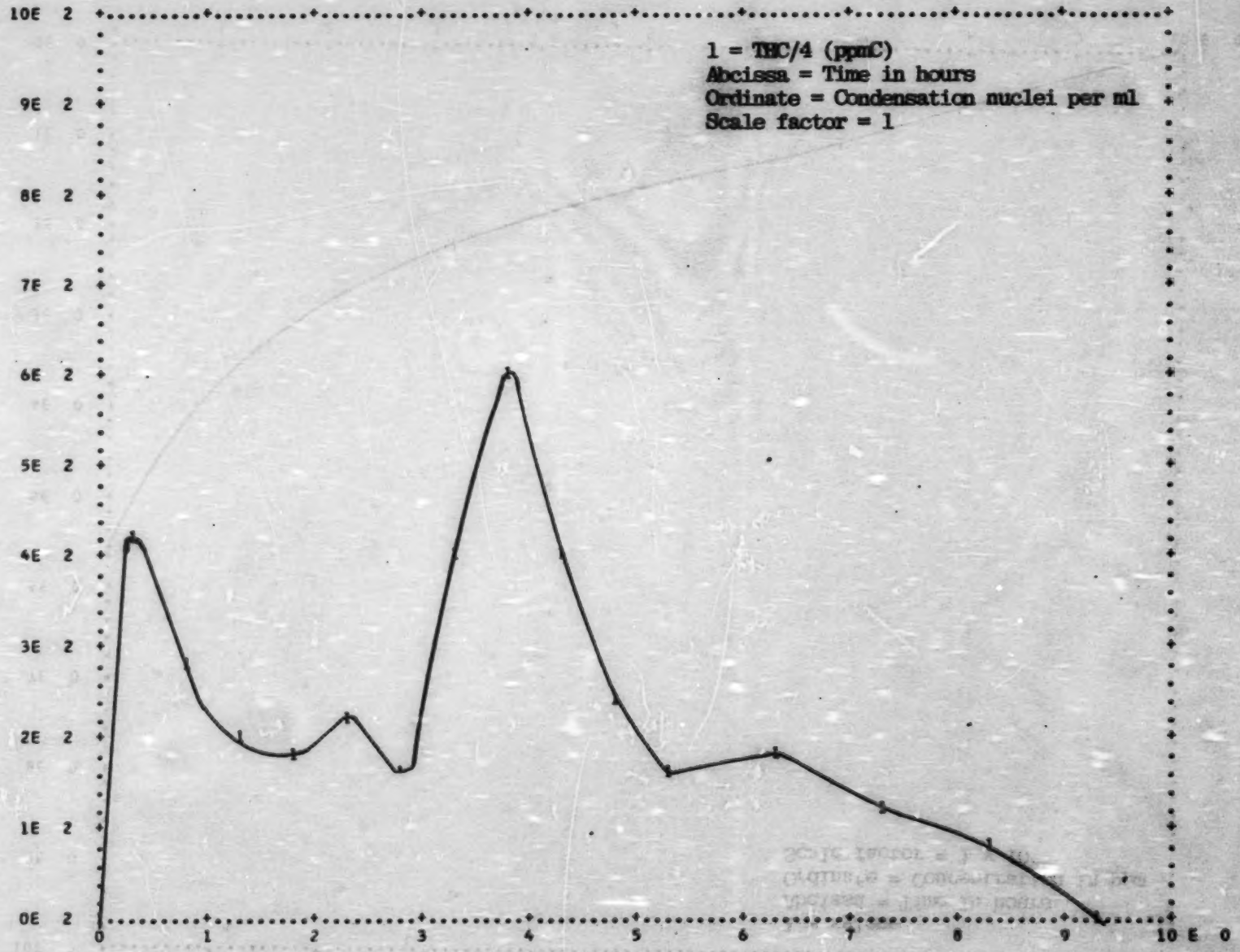
Average Hydrocarbon Disappearance Rates:

(1) ethylene = 0.0104
(2) propylene = 0.0030
(3) butane = 0.0035
(4) i-pentene = 0.0711
(5) toluene = 0.0075
(6) xylene = 0.0133
(Σ = 0.1088)


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0
1
2
3
4
5
6
7
8
9
10 E 0
1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 1
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0
1
2
3
4
5
6
7
8
9
10 E 0

RUN NO. 34: 4 ppm XL-263, 0.5 ppm NO_x, 0.15 ppm NO_2, DILUTION
AUGUST 18, 1975

Average Temperature = 33.50 ± 0.26 °C

Average Dilution Rate = $0.584 \times 10^{-1} \pm 0.153 \times 10^{-1}$ hr^{-1} chamber volumes.

NO_2 Photolysis Rate Constant = 0.59 min^{-1}

NO_2 Formation Rate = 0.11 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 1.775 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0.02 ppm hr^{-1}

Average Rate of O_3 Formation = 0.02 ppm hr^{-1}

O_3 Dose = 0.741 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.30 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.30 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0.11 ppm

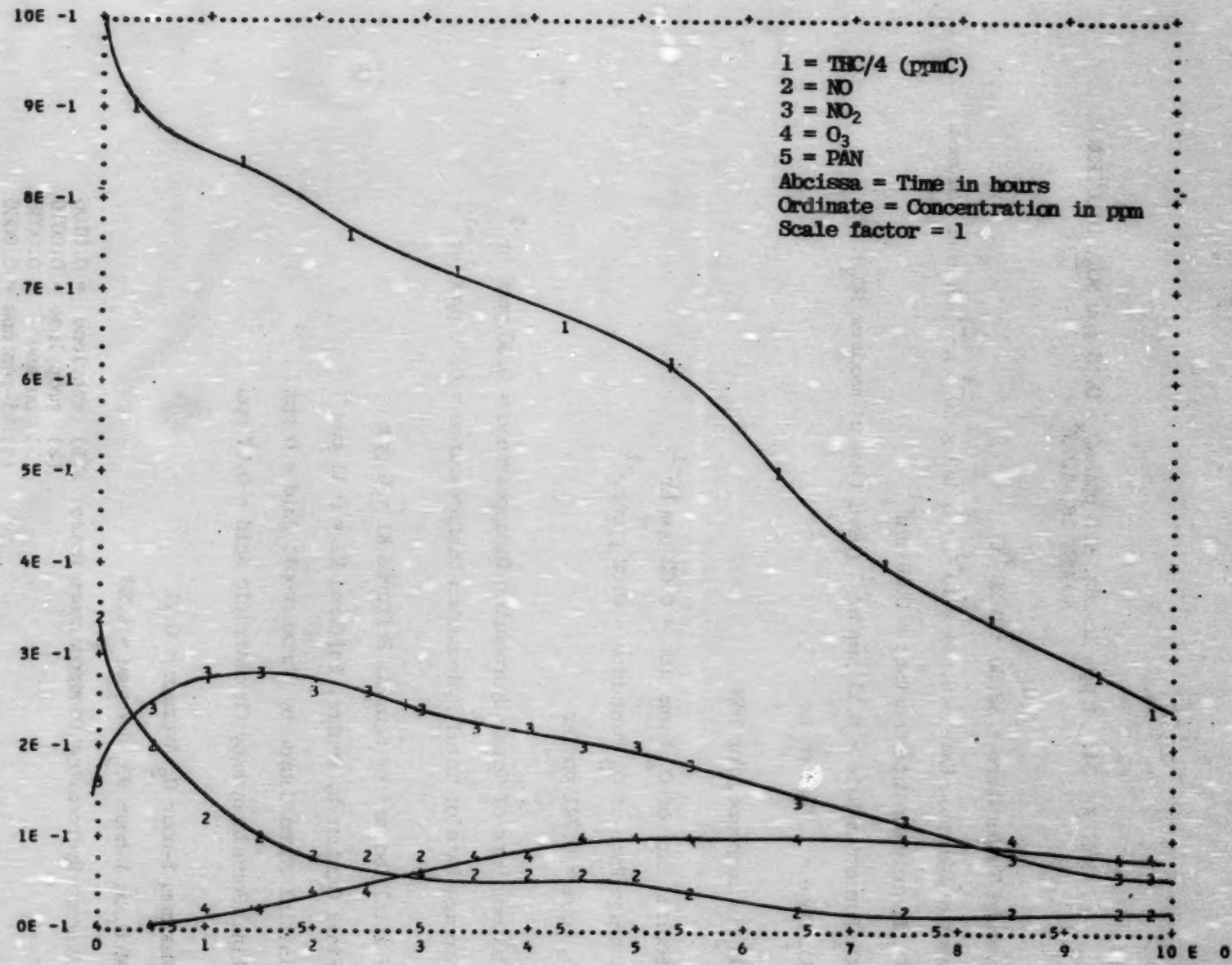
Initial Formaldehyde by Chromatropic Acid = 0 ppm

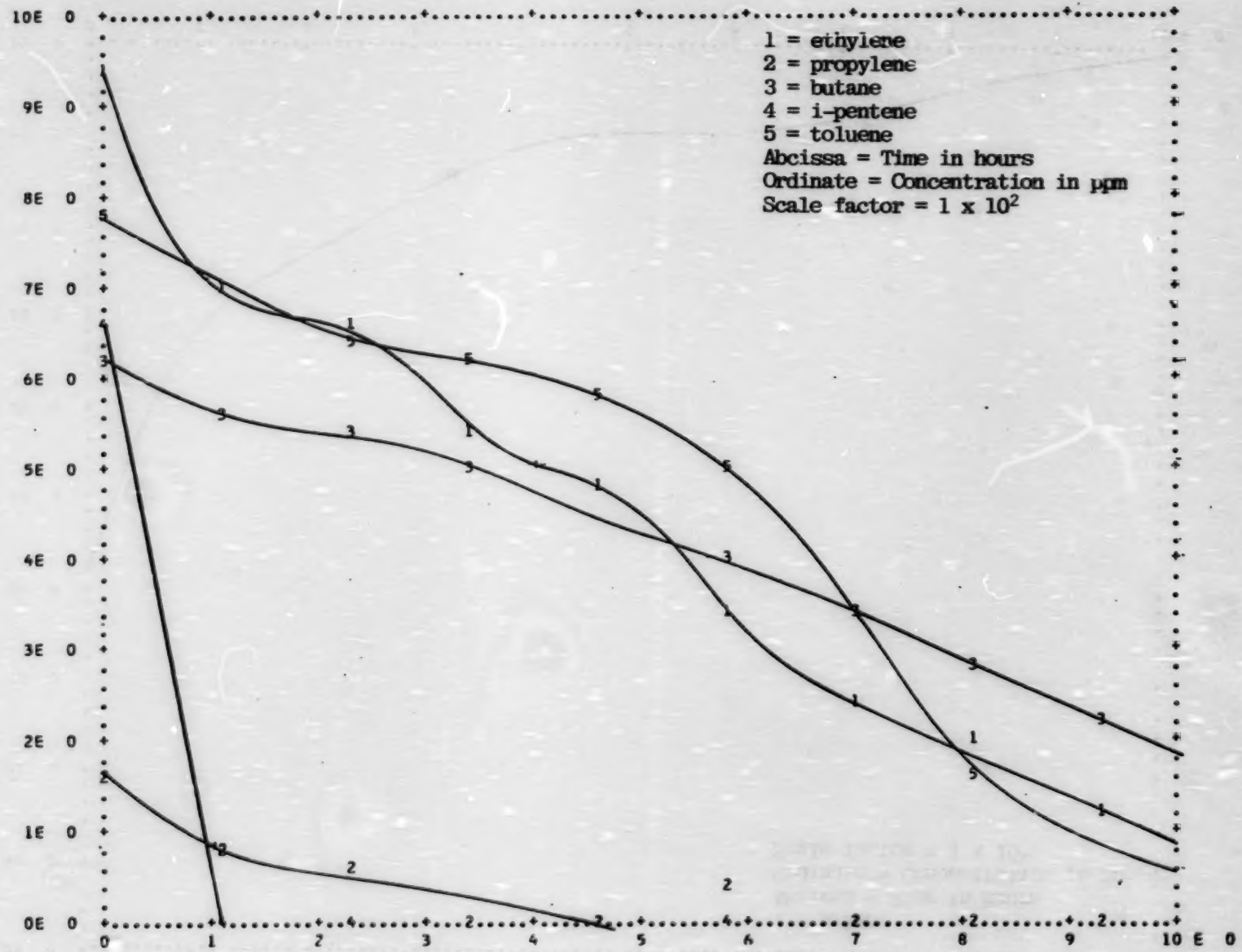
Final Formaldehyde by Chromatropic Acid = 0.07 ppm

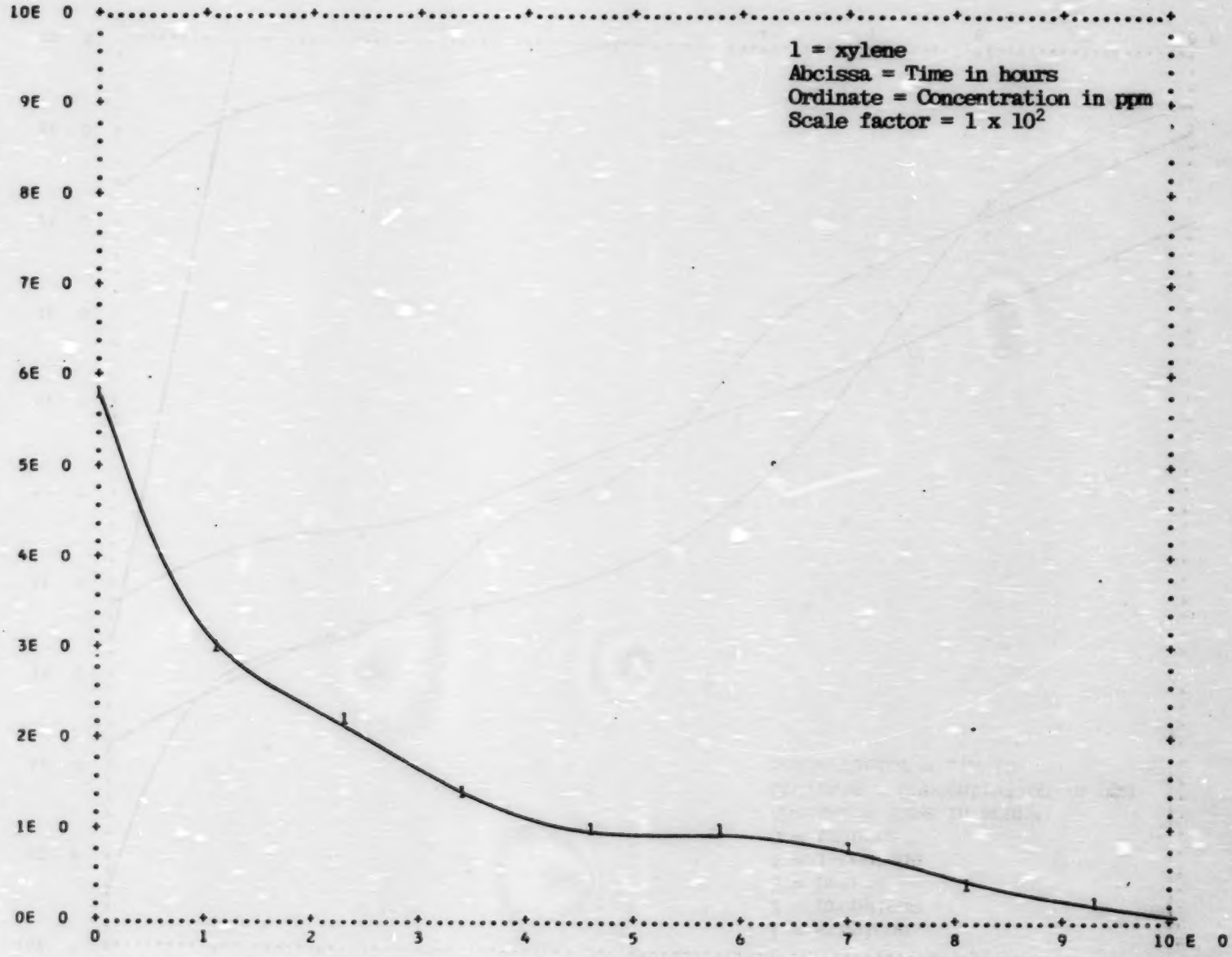
Maximum 1-hour O_3 Average = 0.11

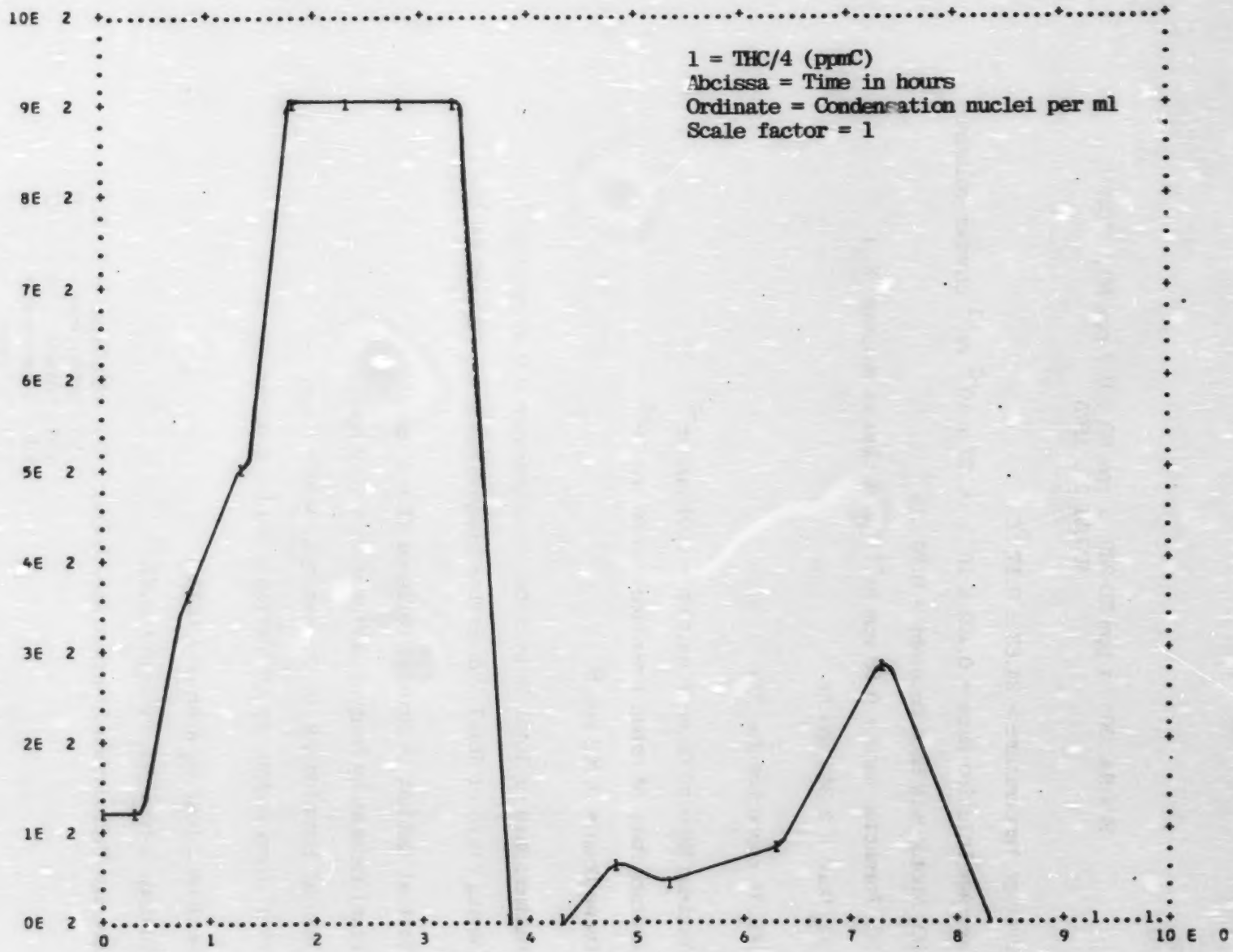
Maximum 1-hour NO_2 Average = 0.28

Average Hydrocarbon Disappearance Rates:
(1) ethylene = 0.0106
(2) propylene = 0.0076
(3) butane = 0.0038
(4) i-pentene = 0.0660
(5) toluene = 0.0055
(6) xylene = 0.0241


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 1
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0 1 2 3 4 5 6 7 8 9 10 E 0

RUN NO. 36: 4 ppm XL-263, 1 ppm NO_x, 0.3 ppm NO_2, DYNAMIC
AUGUST 26, 1975

Average Temperature = 34.63 ± 0.17 °C

Average Dilution Rate = $0.102 \times 10^{0} \pm 0.127 \times 10^{-2}$ hr^{-1} chamber volumes

NO_2 Photolysis Rate Constant = 0.70 min^{-1}

NO_2 Formation Rate = 0.53 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 2.344 ppm hr

NO_2 is corrected for PAN

Maximum Rate of Ozone Formation = 0.04 ppm hr^{-1}

Average Rate of Ozone Formation = 0.06 ppm hr^{-1}

Ozone Dose = 0.903 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.47 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.88 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0.03 ppm

Initial Formaldehyde by Chromatropic Acid = 0 ppm

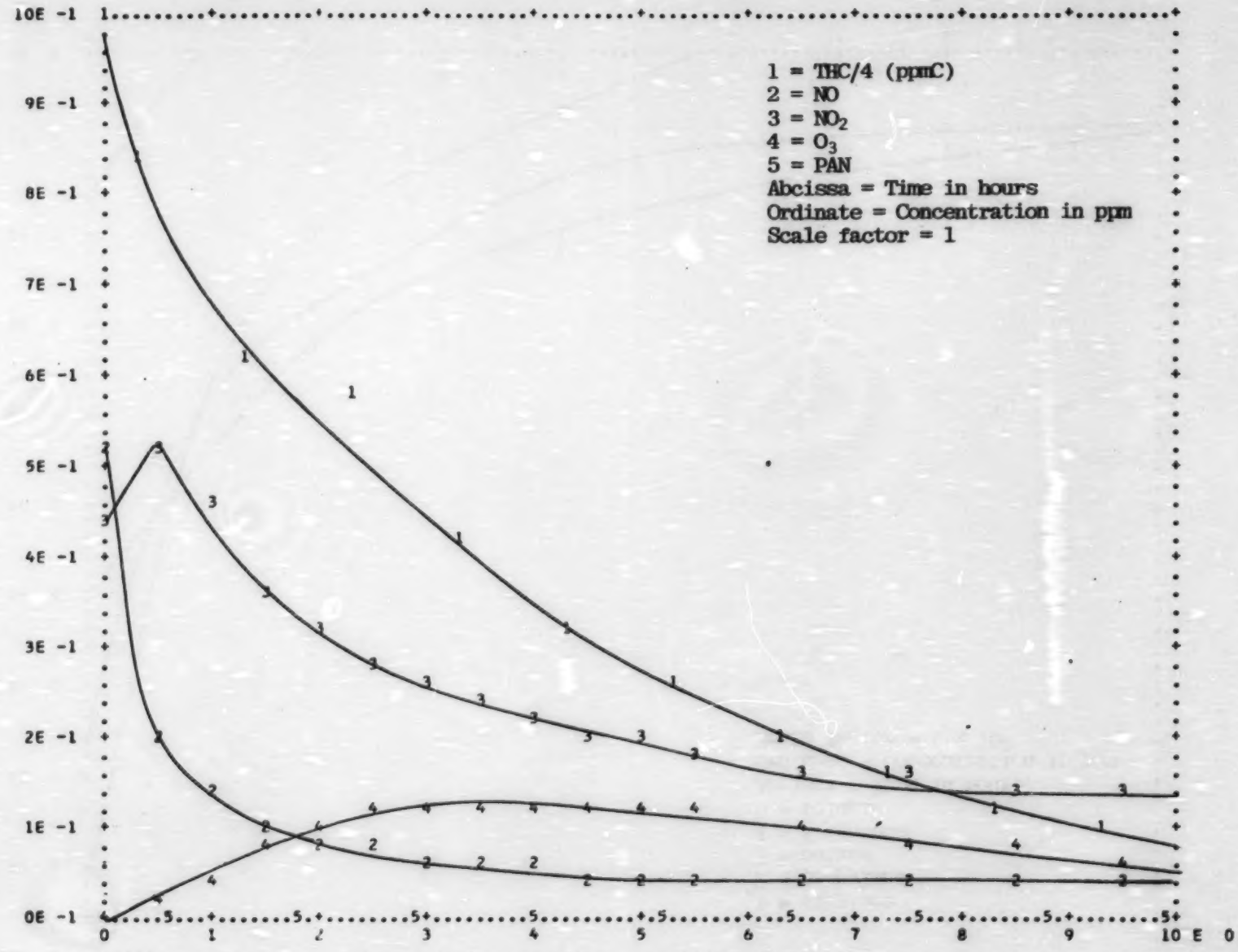
Final Formaldehyde by Chromatropic Acid = 0.05 ppm

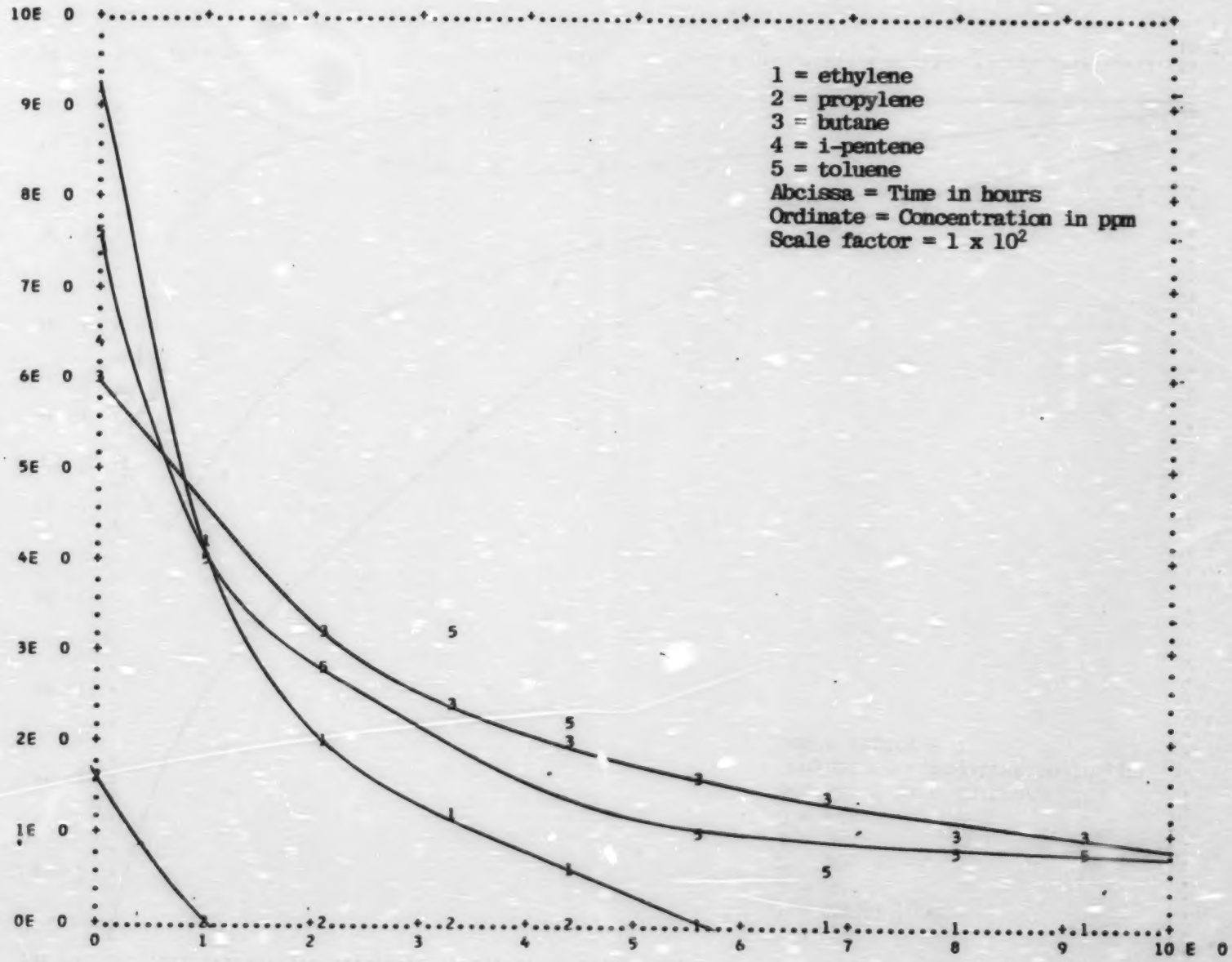
Maximum 1-hour O_3 Average = 0.13

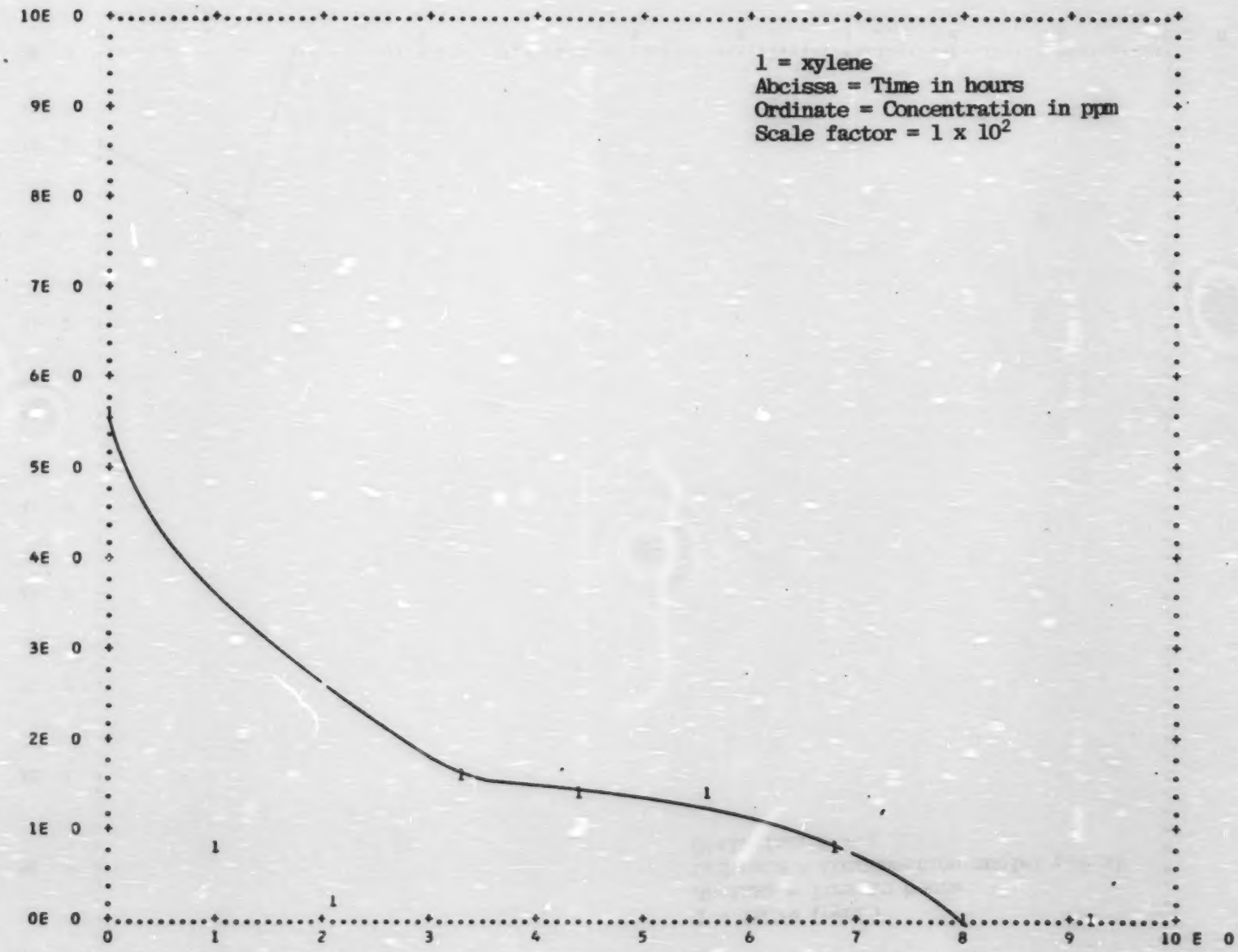
Maximum 1-hour NO_2 Average = 0.47

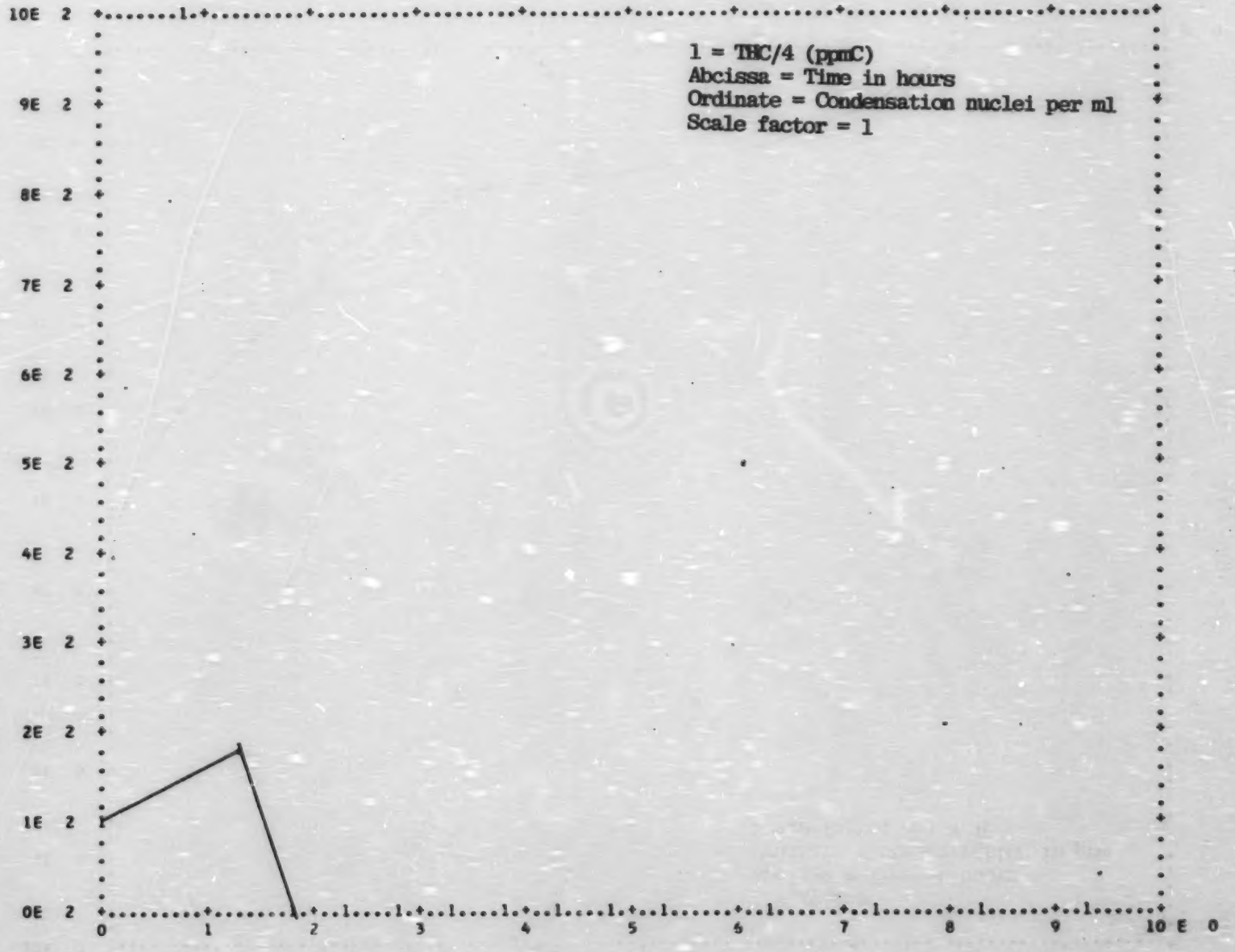
Average Hydrocarbon Disappearance Rates:

(1) ethylene = 0.0511
(2) propylene = 0.0200
(3) butane = 0.0127
(4) i-pentene = (+00)
(5) toluene = 0.0340
(6) xylene = 0.0151


1 = THC/4 (ppmC)
2 = NO
3 = NO_2
4 = O_3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10^2
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 1
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0 1 2 3 4 5 6 7 8 9 10 E 0

RUN NO. 37: 4 ppm XL-263, 0.5 ppm NO_x, 0.15 ppm NO_2, DYNAMIC
AUGUST 28, 1975

Average Temperature = 32.88 ± 0.20 °C

Average Dilution Rate = $0.106 \times 10^{0} \pm 0.277 \times 10^{-2}$ hr^{-1} chamber volumes

NO_2 Photolysis Rate Constant = 0.44 min^{-1}

NO_2 Formation Rate = 0.30 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 2.335 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0.04 ppm hr^{-1}

Average Rate of O_3 Formation = 0.04 ppm hr^{-1}

O_3 Dose = 0.230 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.43 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.78 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0.03 ppm

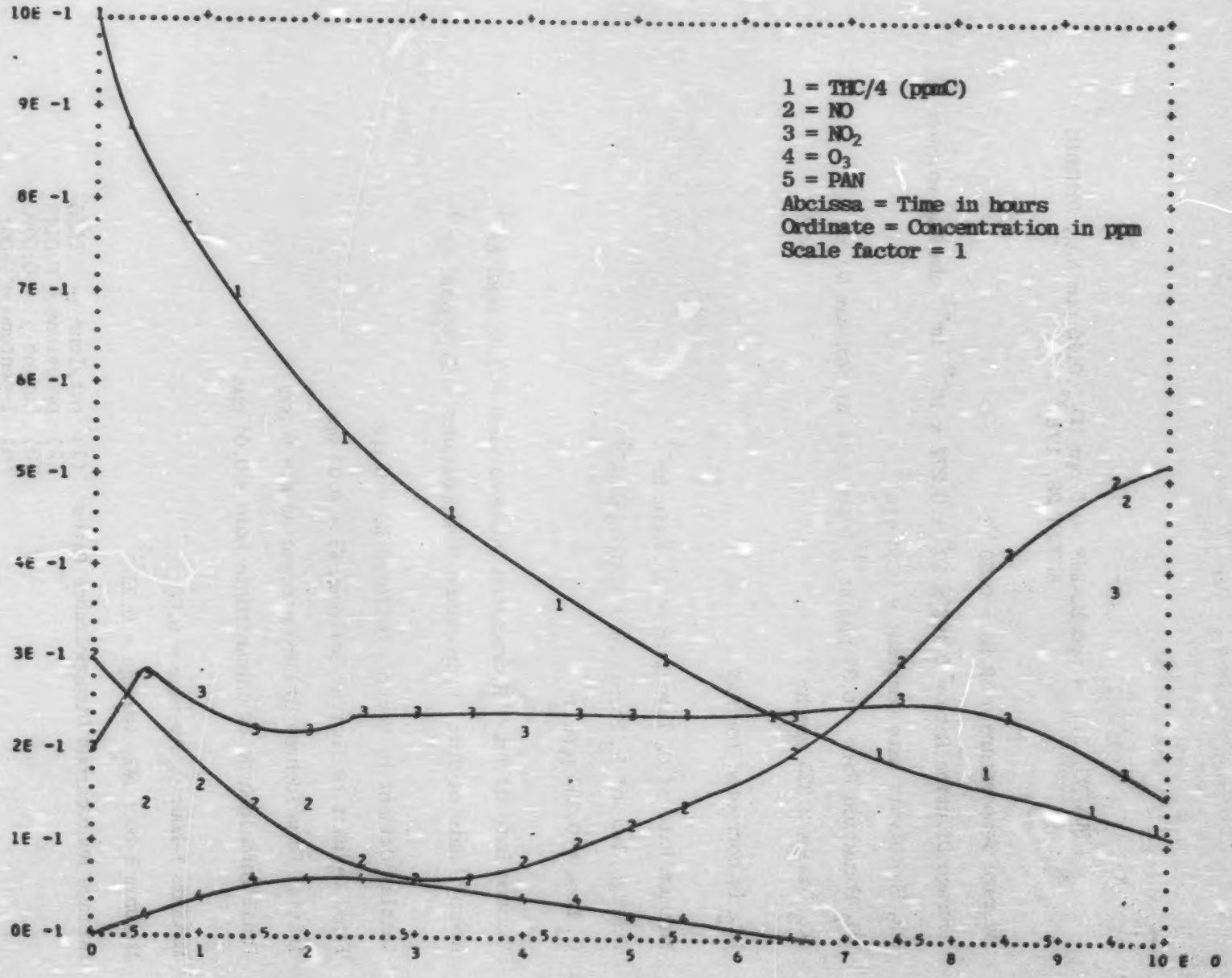
Initial Formaldehyde by Chromatropic Acid = 0 ppm

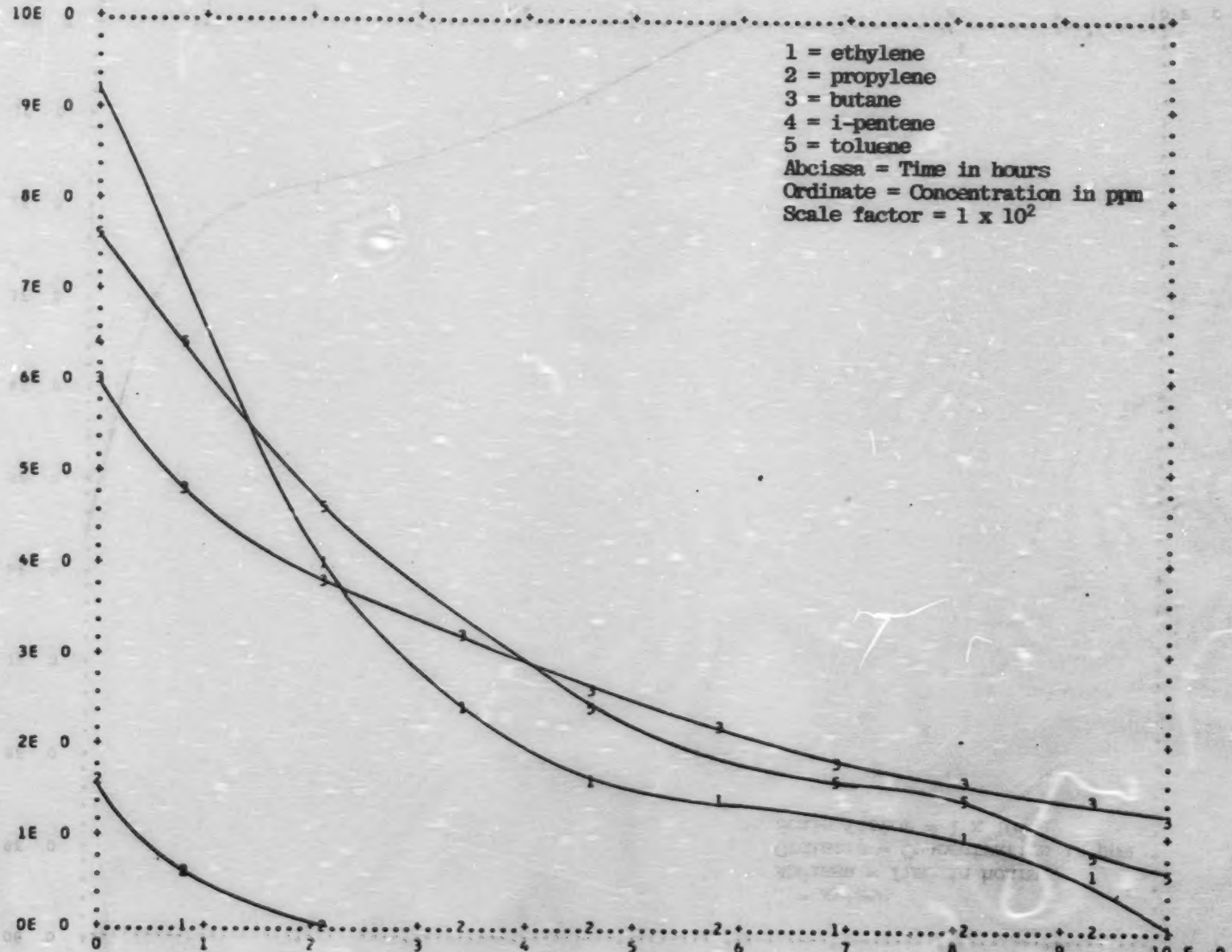
Final Formaldehyde by Chromatropic Acid = 0.04 ppm

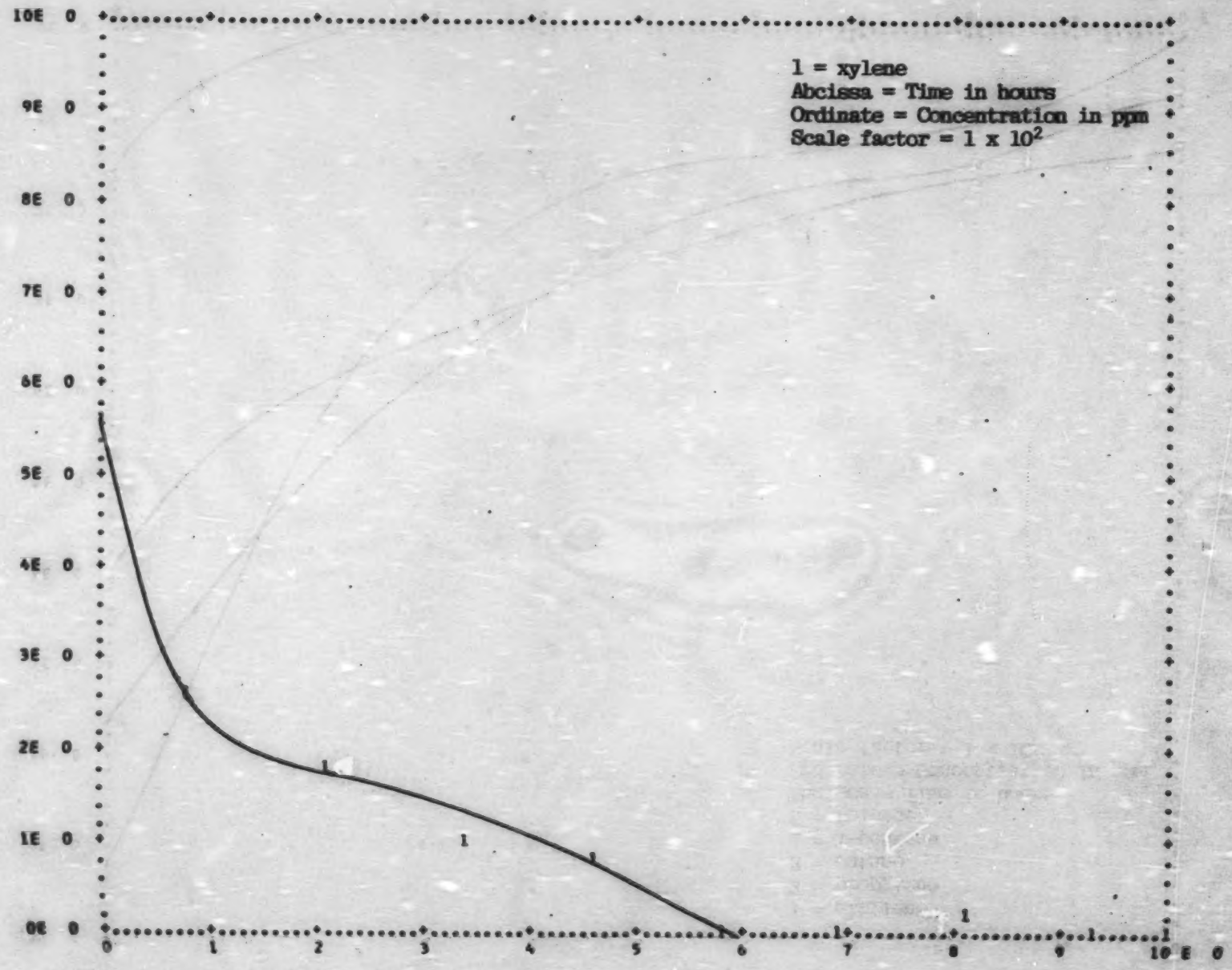
Maximum 1-hour O_3 Average = 0.06

Maximum 1-hour NO_2 Average = 0.25

Average Hydrocarbon Disappearance Rates:
(1) ethylene = 0.0255
(2) propylene = 0.0145
(3) butane = 0.0092
(4) i-pentene = (→00)
(5) toluene = 0.0134
(6) xylene = 0.0400


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0
1
2
3
4
5
6
7
8
9
10 E 0


10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0
1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0

RUN NO. 39: 2 ppm XL-263, 1 ppm NO_x, 0.3 ppm NO_2, STATIC
SEPTEMBER 4, 1975

Average Temperature = 33.13 ± 0.27 °C

Average Dilution Rate = $0.138 \times 10^{-1} \pm 0.103 \times 10^{-2}$ hr^{-1} chamber volumes

Concentrations are corrected for dilution

NO_2 Photolysis Rate Constant = Cannot calculate.
No intersection of NO and O_3 curves.

NO_2 Formation Rate = Cannot calculate.
Zero in denominator .

NO_2 Dose = 3.584 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0 ppm hr^{-1}

Average Rate of O_3 Formation = 0 ppm hr^{-1}

O_3 Dose = 0.003 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.07 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.12 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0 ppm

Initial Formaldehyde by Chromatropic Acid = 0 ppm

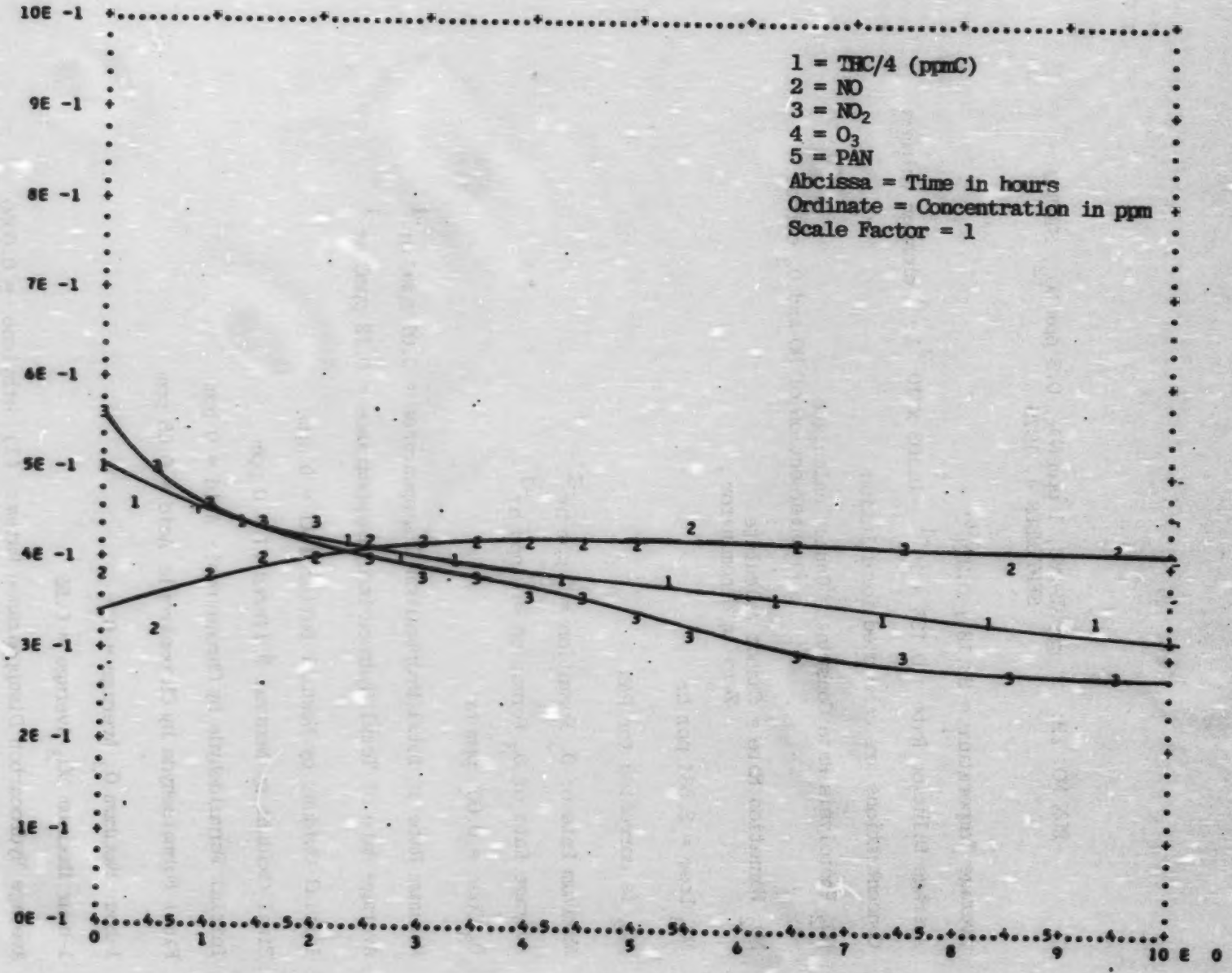
Final Formaldehyde by Chromatropic Acid = 0.05 ppm

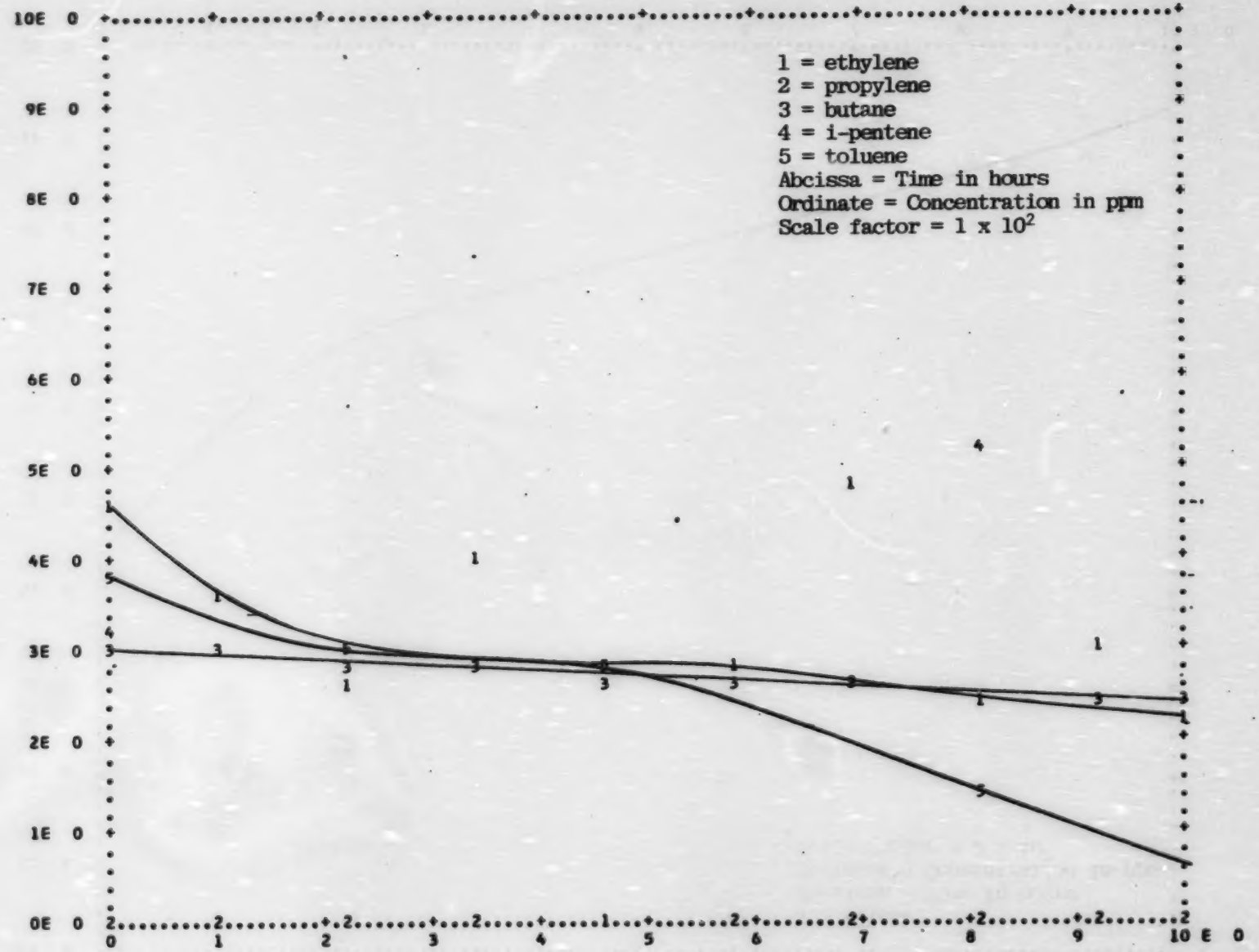
1-hour Maximum O_3 Average = 0

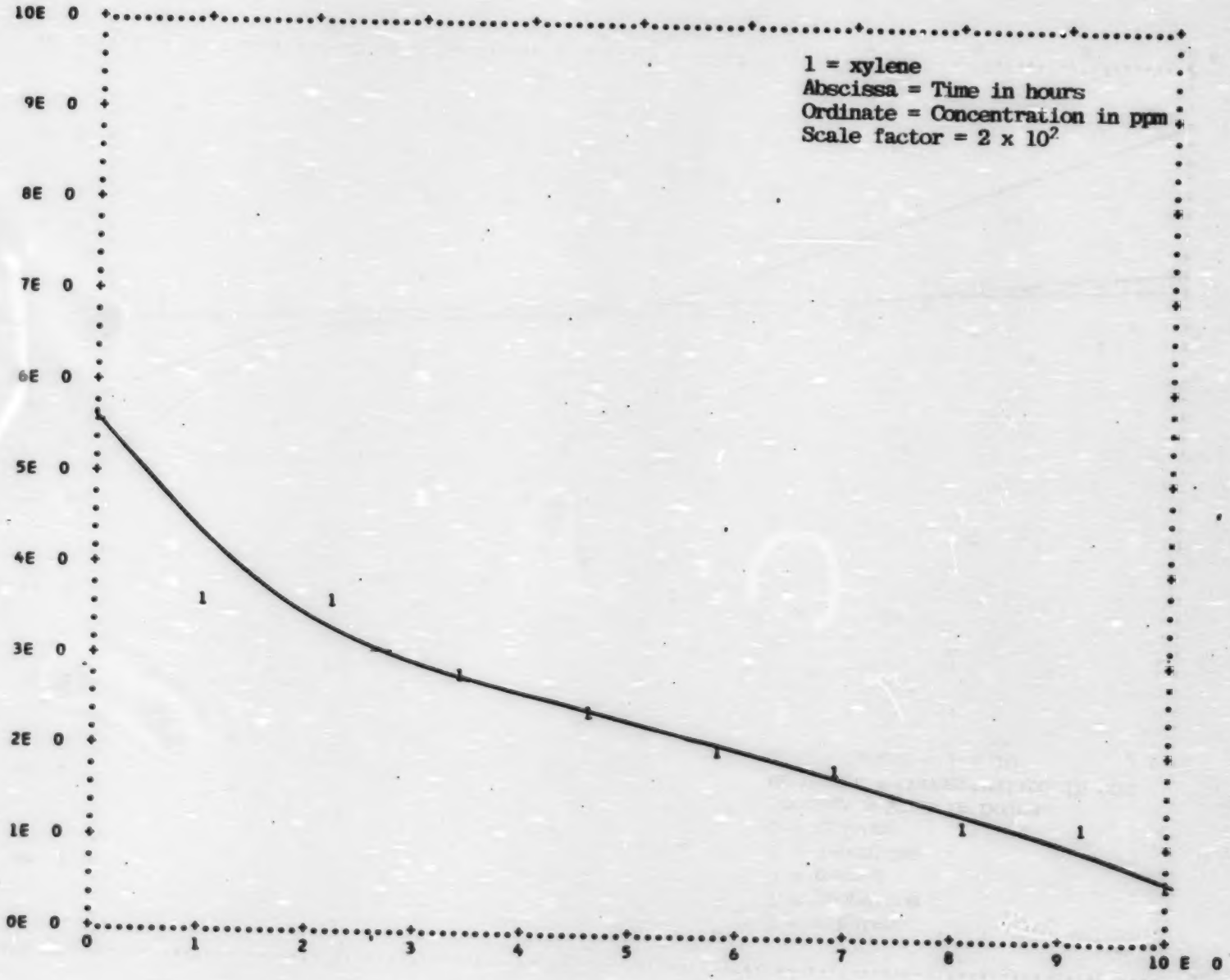
1-hour Maximum NO_2 Average = 0.53

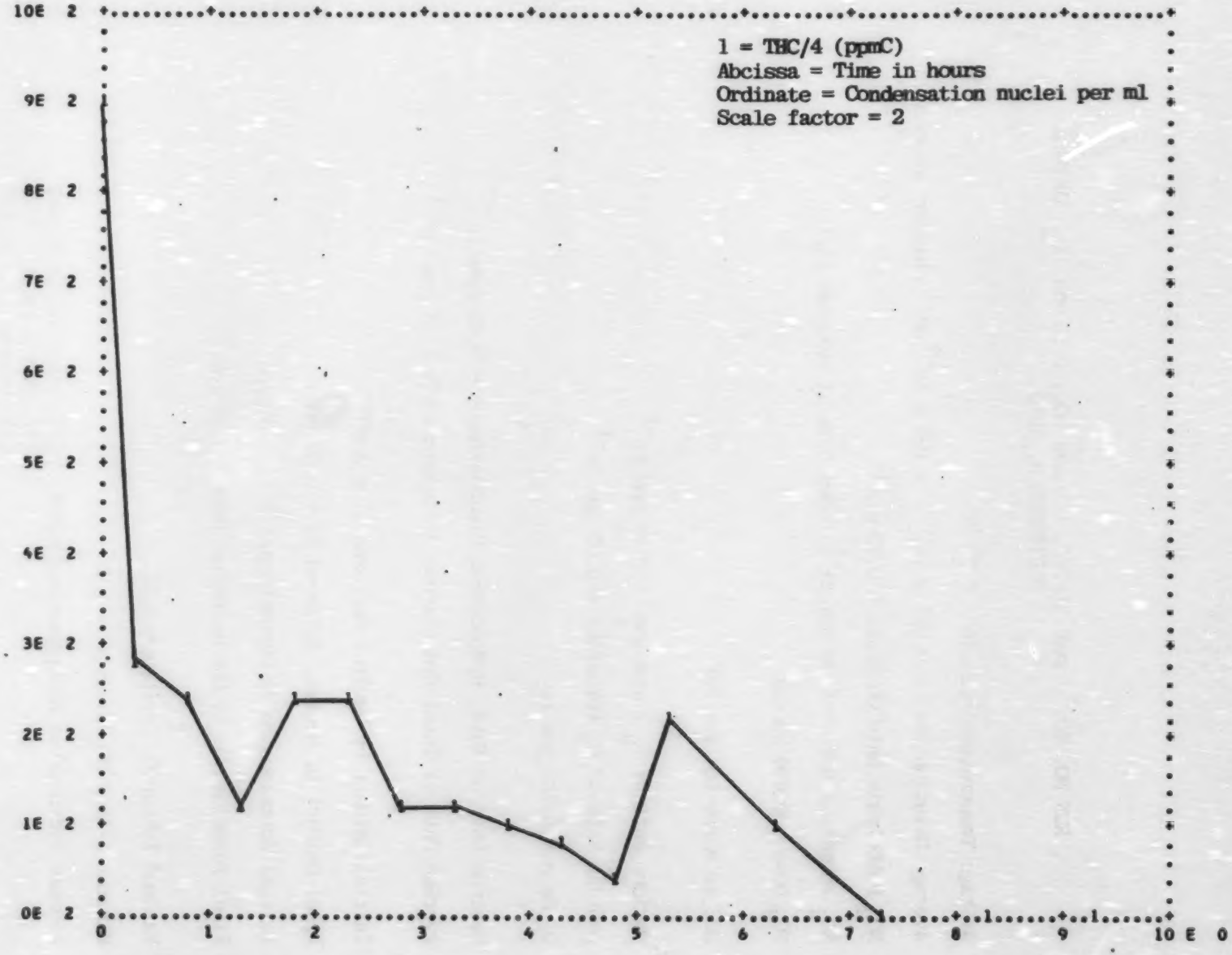
Average Hydrocarbon Disappearance Rates:

(1)	ethylene	= 0.0050
(2)	propylene	= -
(3)	butane	= 0.0005
(4)	i-pentene	= -
(5)	toluene	= 0.0024
(6)	xylene	= 0.0046


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale Factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abscissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 2 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0
1
2
3
4
5
6
7
8
9
10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 2
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0
1
2
3
4
5
6
7
8
9
10 E 0

RUN NO. 40: 4 ppm XL-263, 0.5 ppm NO_x, 0.15 ppm NO_2, DYNAMIC
SEPTEMBER 8, 1975

Average Temperature = 33.18 ± 0.23 °C

Average Dilution Rate = $0.927 \times 10^{-1} \pm 0.159 \times 10^{-2}$ hr^{-1} chamber volumes

NO_2 Photolysis Rate Constant = 0.73 min^{-1}

NO_2 Formation Rate = 0.36 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 0.694 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0.03 ppm hr^{-1}

Average Rate of O_3 Formation = 0.05 ppm hr^{-1}

O_3 Dose = 0.764 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.40 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 1.13 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0.03 ppm

Initial Formaldehyde by Chromatropic Acid = 0 ppm

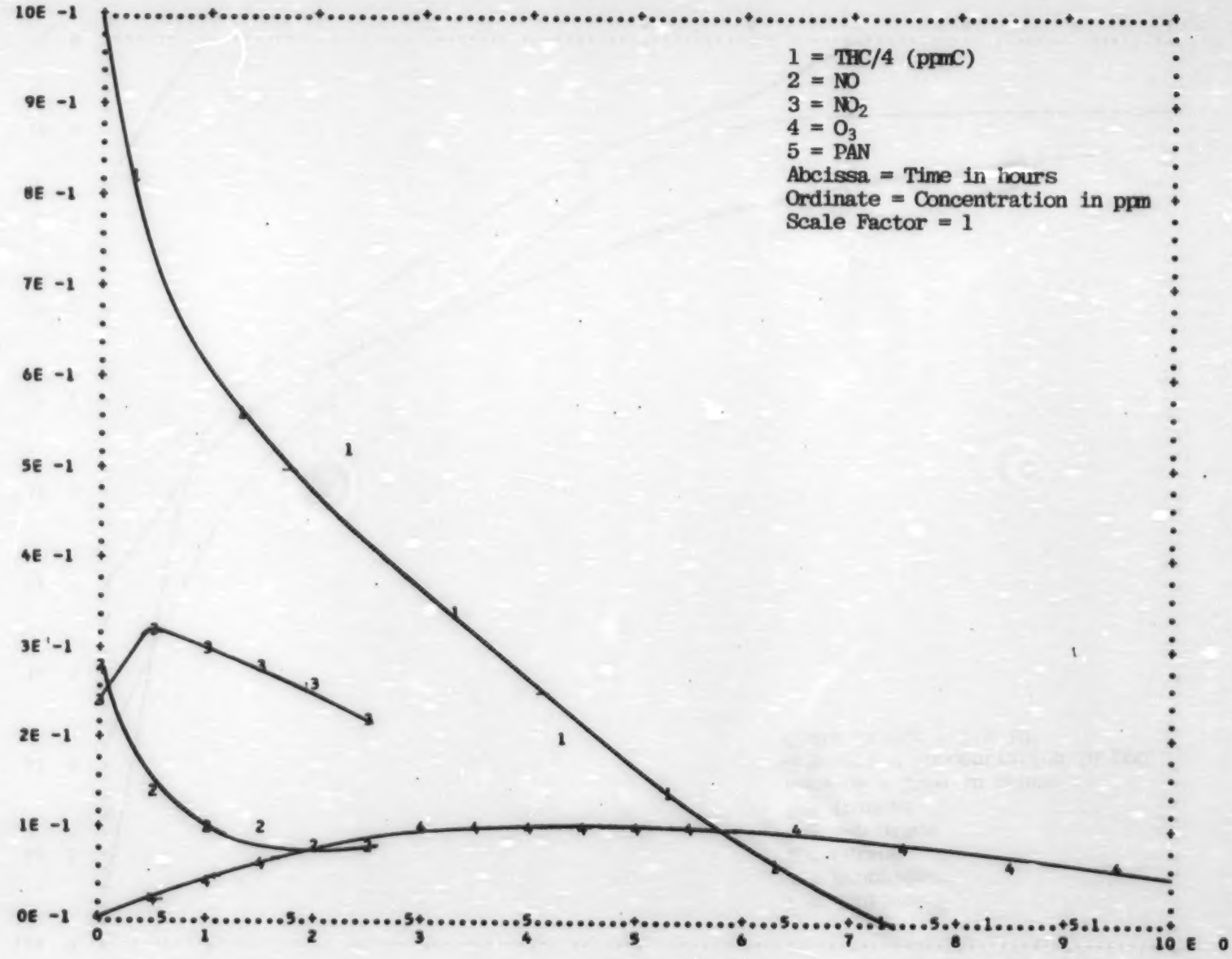
Final Formaldehyde by Chromatropic Acid = 0.04 ppm

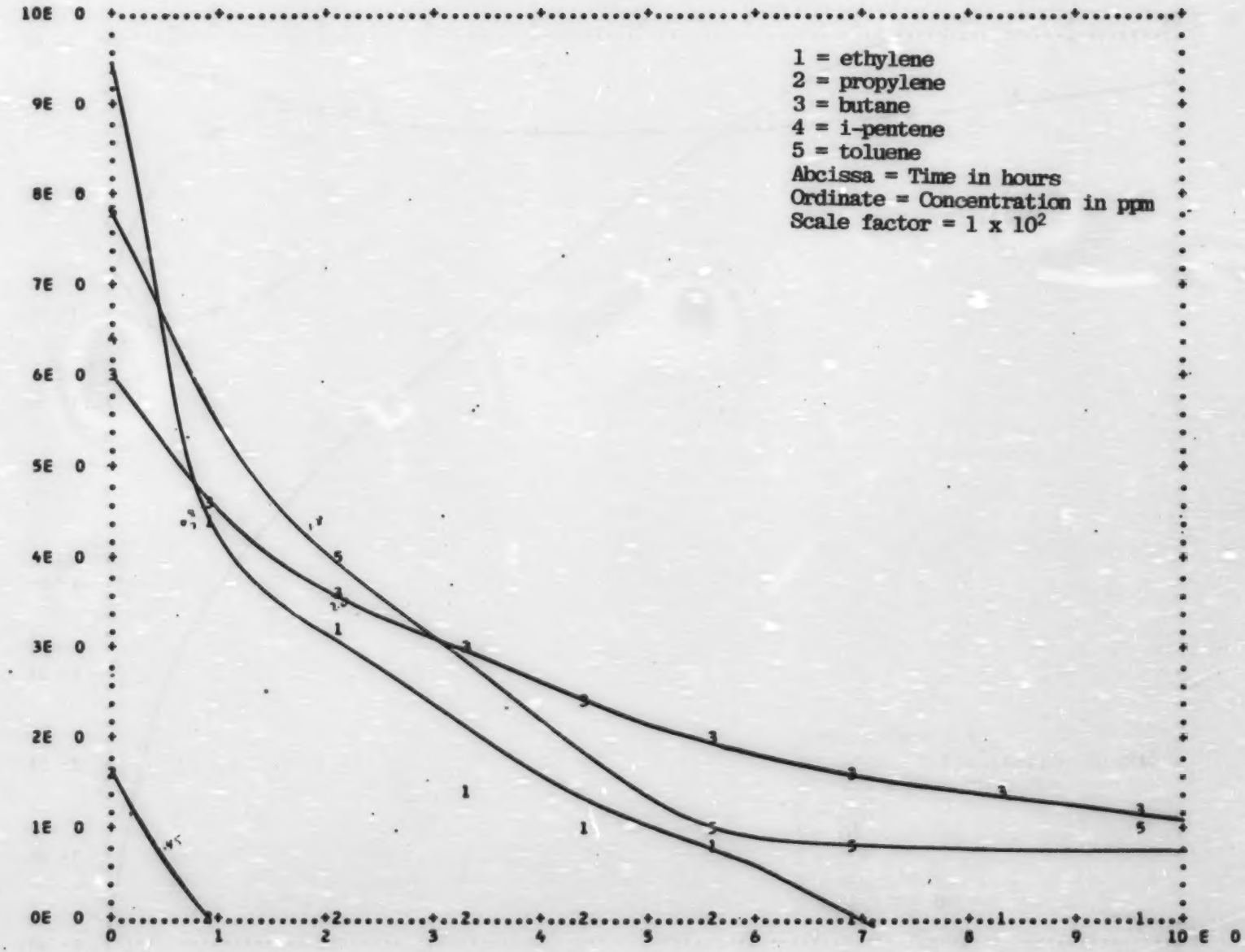
Maximum 1-hour O_3 Average = 0.10

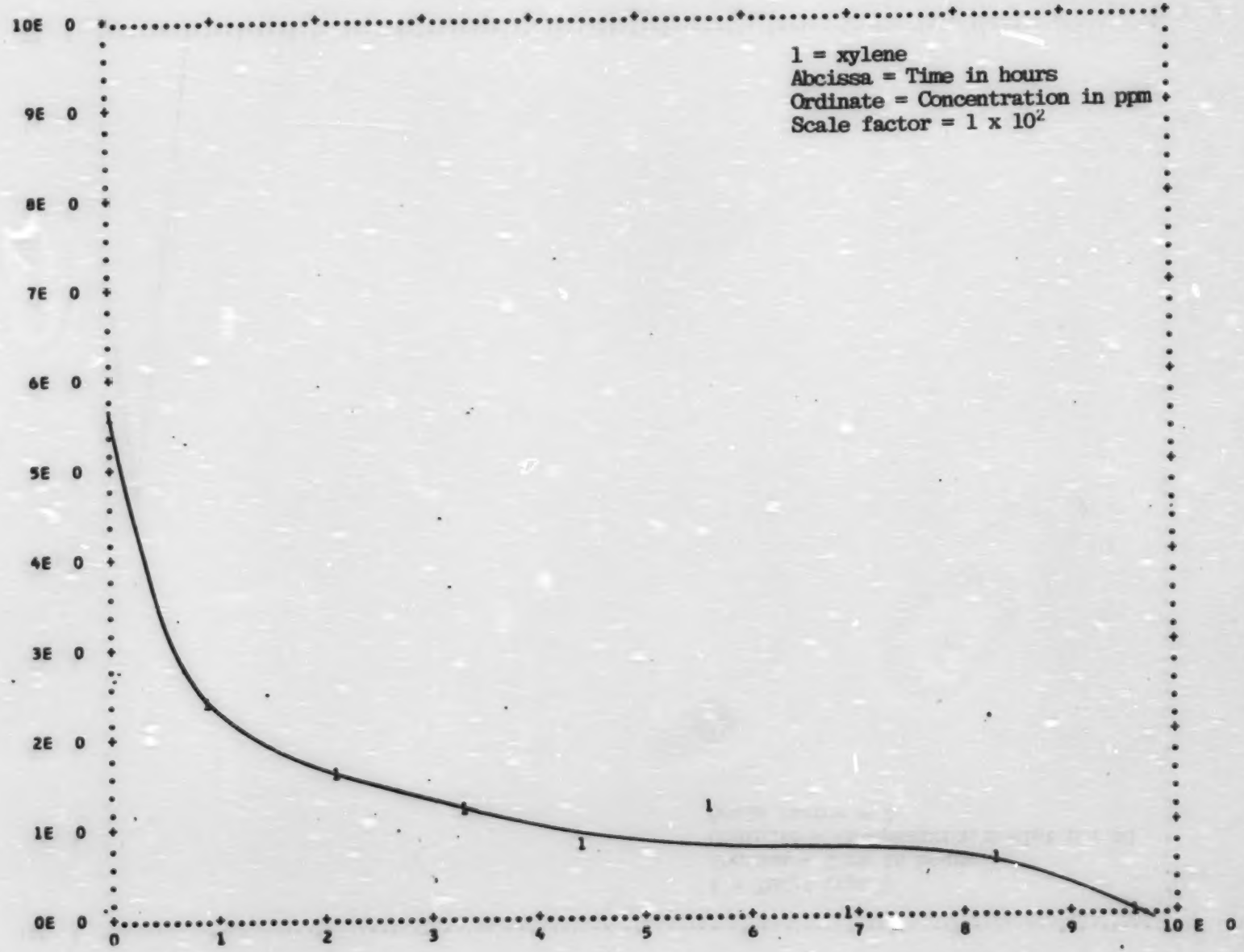
Maximum 1-hour NO_2 Average = 0.22

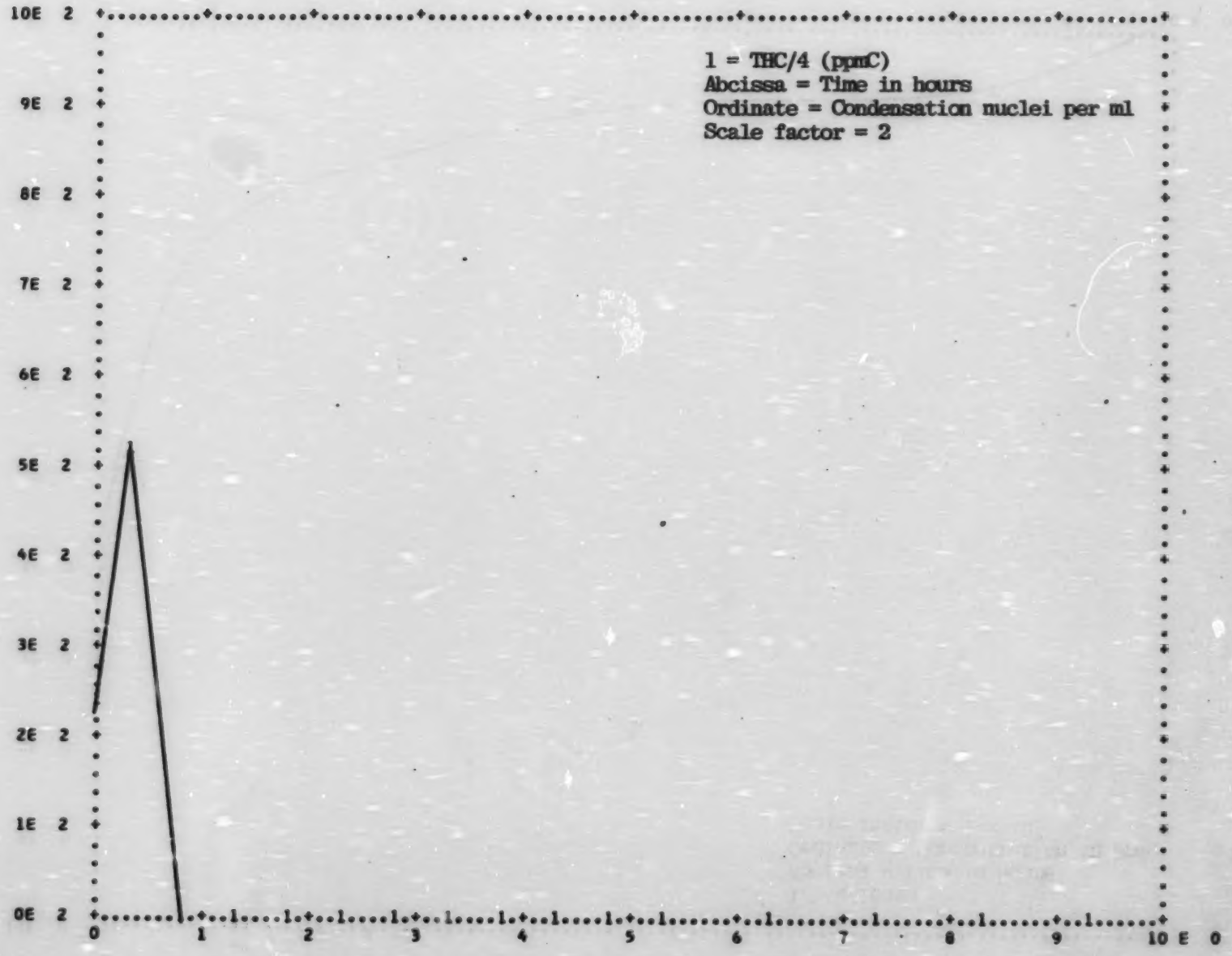
Average Hydrocarbon Disappearance Rates:

(1)	ethylene	= 0.0587
(2)	propylene	= 0.0177
(3)	butane	= 0.0122
(4)	i-pentene	= -
(5)	toluene	= 0.0188
(6)	xylene	= 0.0430


10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0
1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale Factor = 1


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 2
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0
1
2
3
4
5
6
7
8
9
10 E 0

RUN NO. 41: 4 ppm XL-263, 0.5 ppm NO_x, 0.15 ppm NO_2, DILUTION
September 17, 1975

Average Temperature = 33.20 ± 0.23 °C

Average Dilution Rate = $0.538 \times 10^{-1} \pm 0.136 \times 10^{-1}$ hr^{-1} chamber volumes

NO_2 Photolysis Rate Constant = Cannot calculate.
No intersection of NO and O_3 curves.

NO_2 Formation Rate = 0.16 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 1.936 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0.50 ppm hr^{-1}

Average Rate of O_3 Formation = 0.04 ppm hr^{-1}

O_3 Dose = 0.105 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.30 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.26 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0.01 ppm

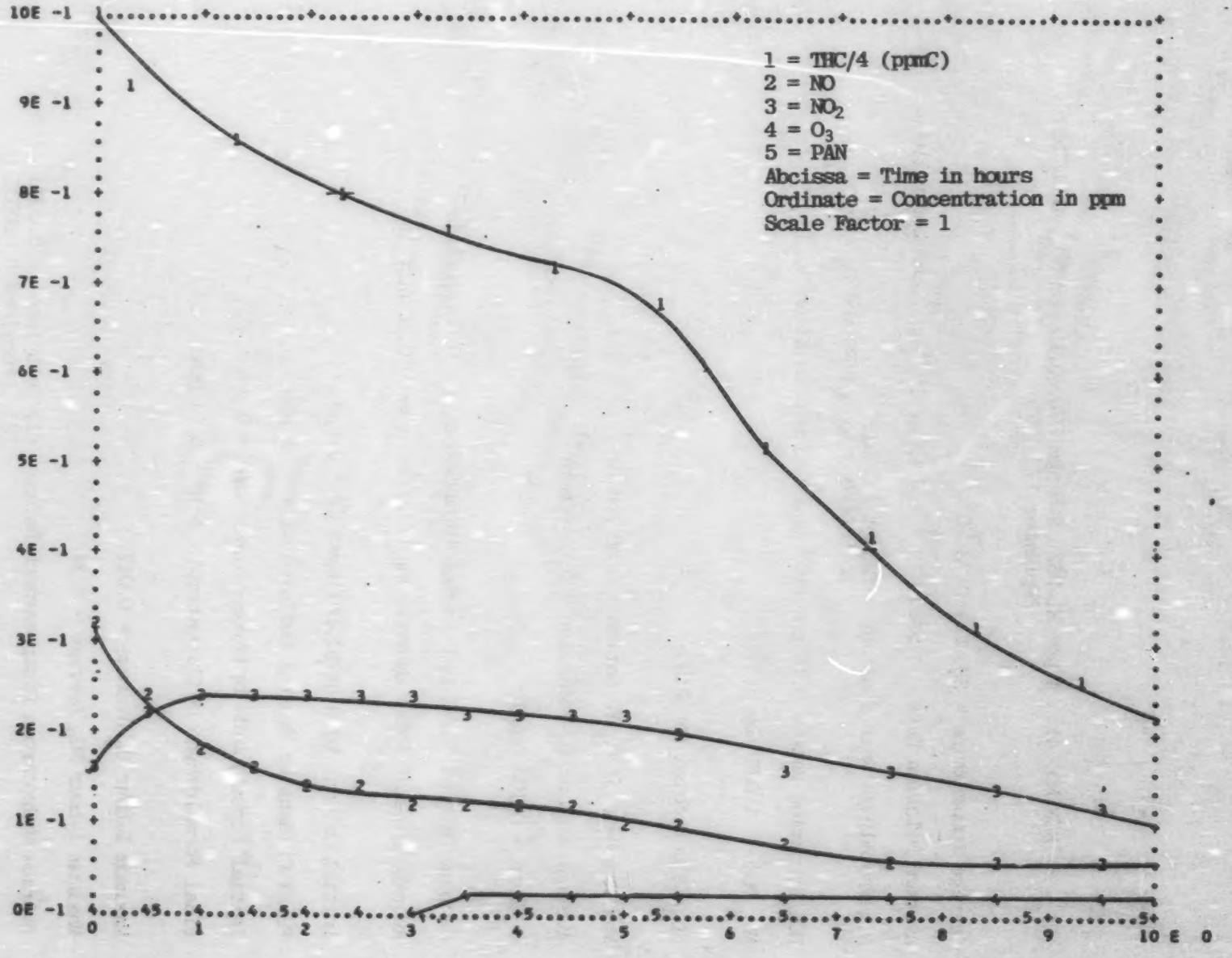
Initial Formaldehyde by Chromatropic Acid = 0 ppm

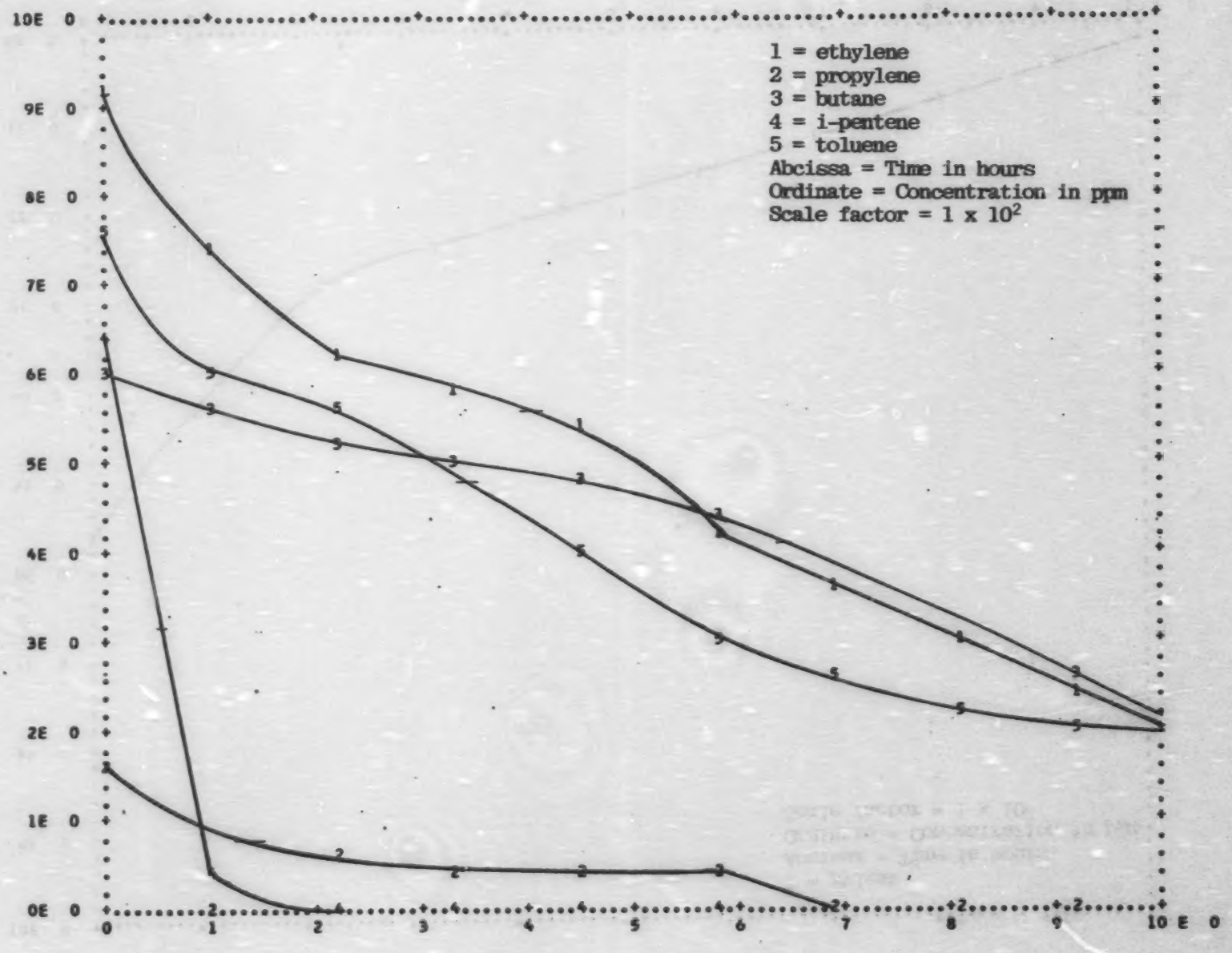
Final Formaldehyde by Chromatropic Acid = 0.04 ppm

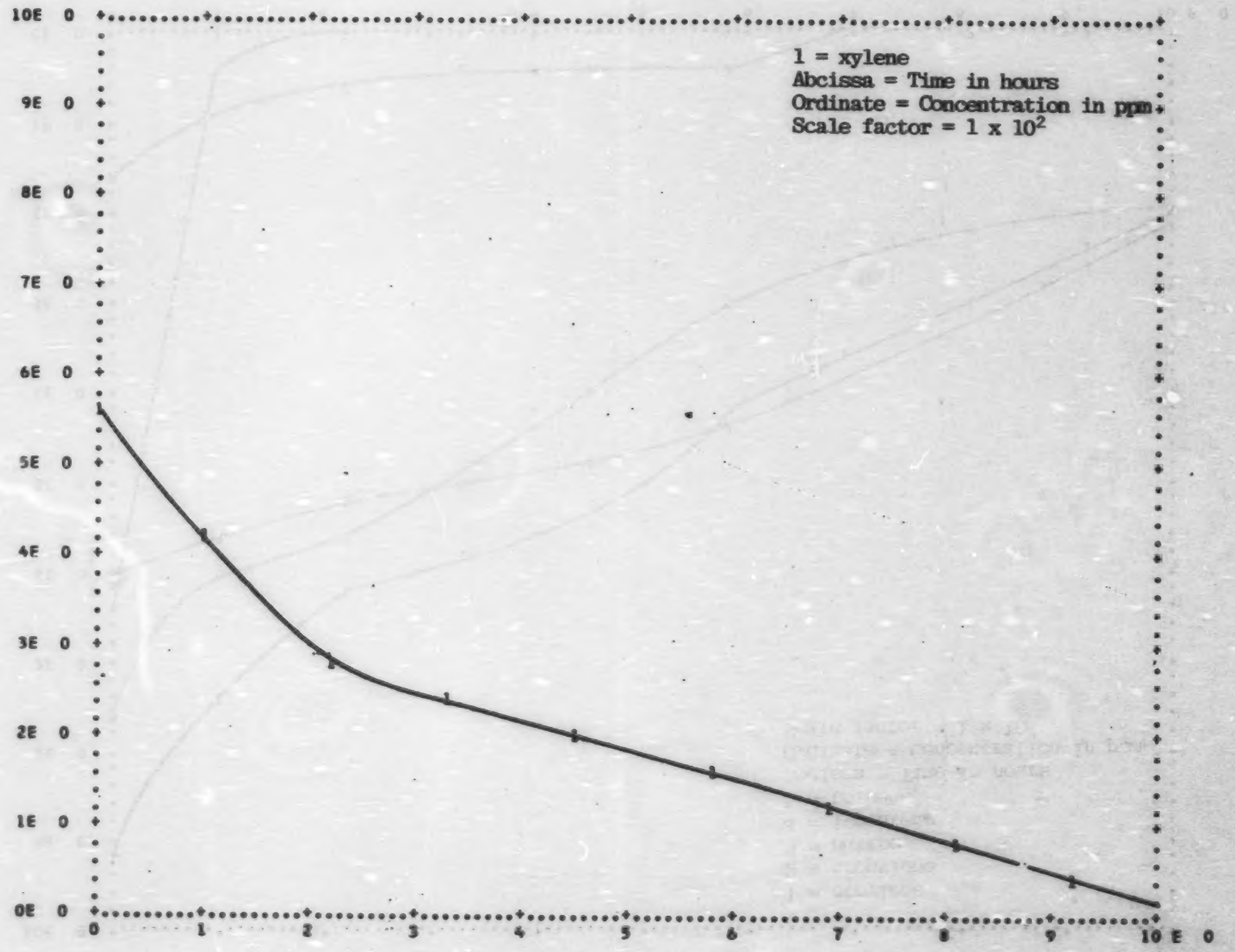
Maximum 1-hour O_3 Average = 0.017

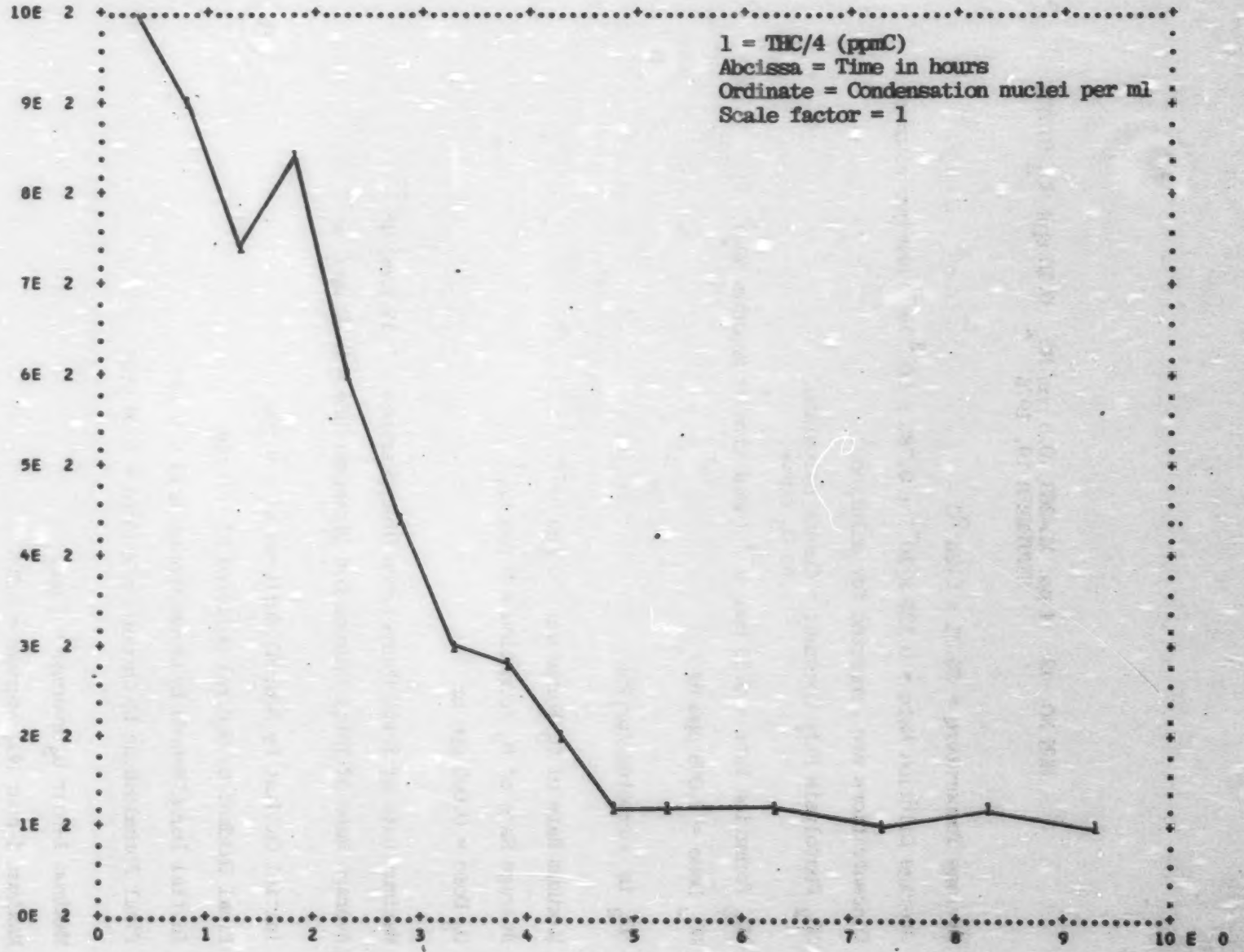
Maximum 1-hour NO_2 Average = 0.24

Average Hydrocarbon Disappearance Rates:
(1) ethylene = 0.0090
(2) propylene = 0.0033
(3) butane = 0.0029
(4) i-pentene = 0.0581
(5) toluene = 0.0081
(6) xylene = 0.0128


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale Factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0
1
2
3
4
5
6
7
8
9
10 E 0
1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 1
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0
1
2
3
4
5
6
7
8
9
10 E 0

RUN NO. 42: 4 ppm XL-263, 0.5 ppm NO_x, 0.15 ppm NO_2 STATIC
SEPTEMBER 19, 1975

Average Temperature = 33.31 ± 0.25 °C

Average Dilution Rate = $0.125 \times 10^{-1} \pm 0.782 \times 10^{-3}$ hr^{-1} chamber volumes

Concentrations are corrected for dilution

NO_2 Photolysis Rate Constant = Cannot calculate.
No O_3 curve.

NO_2 Formation Rate = 0.05 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 2.065 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0 ppm hr^{-1}

Average Rate of O_3 Formation = 0 ppm hr^{-1}

O_3 Dose = 0.060 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.12 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.22 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0 ppm

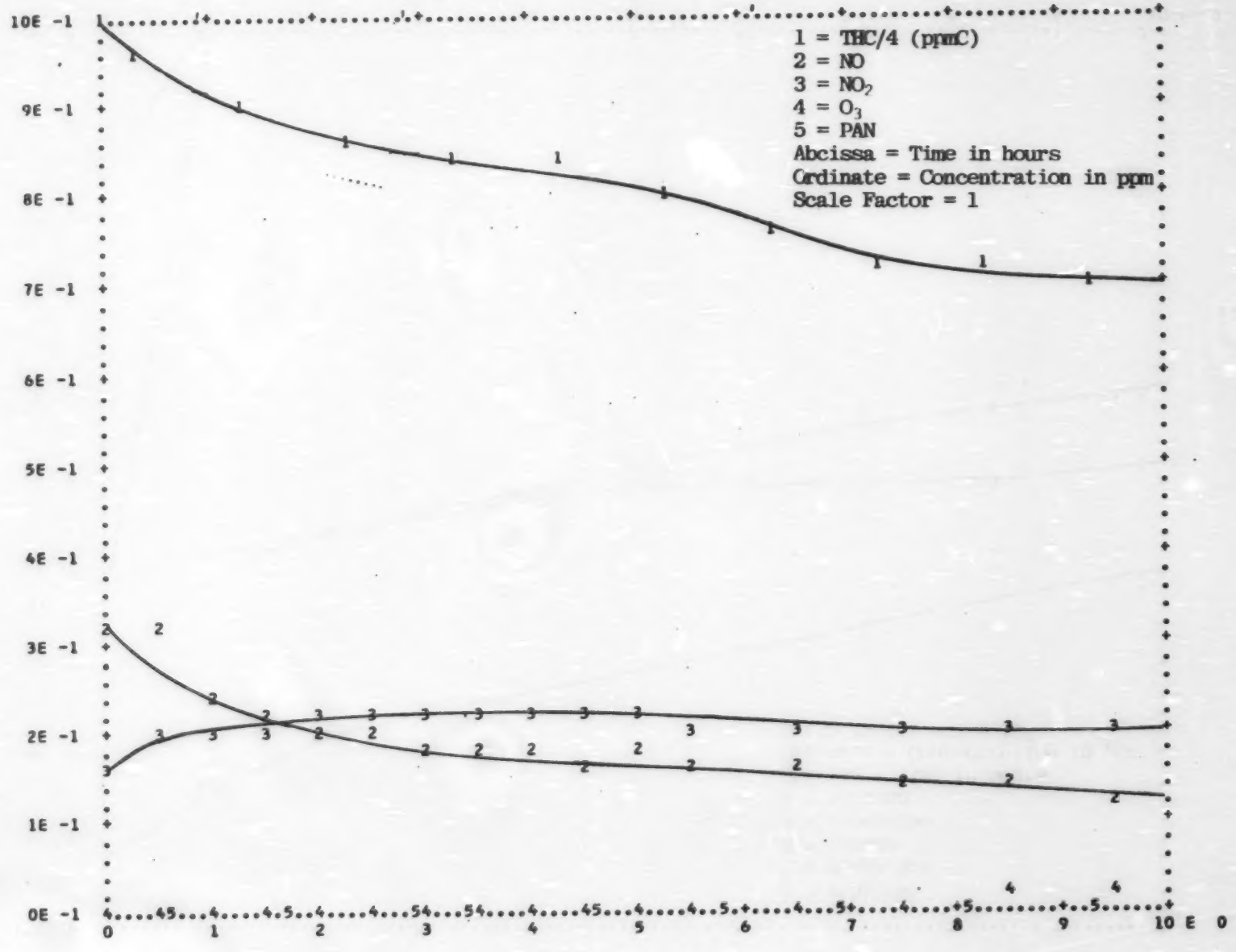
Initial Formaldehyde by Chromatropic Acid = 0 ppm

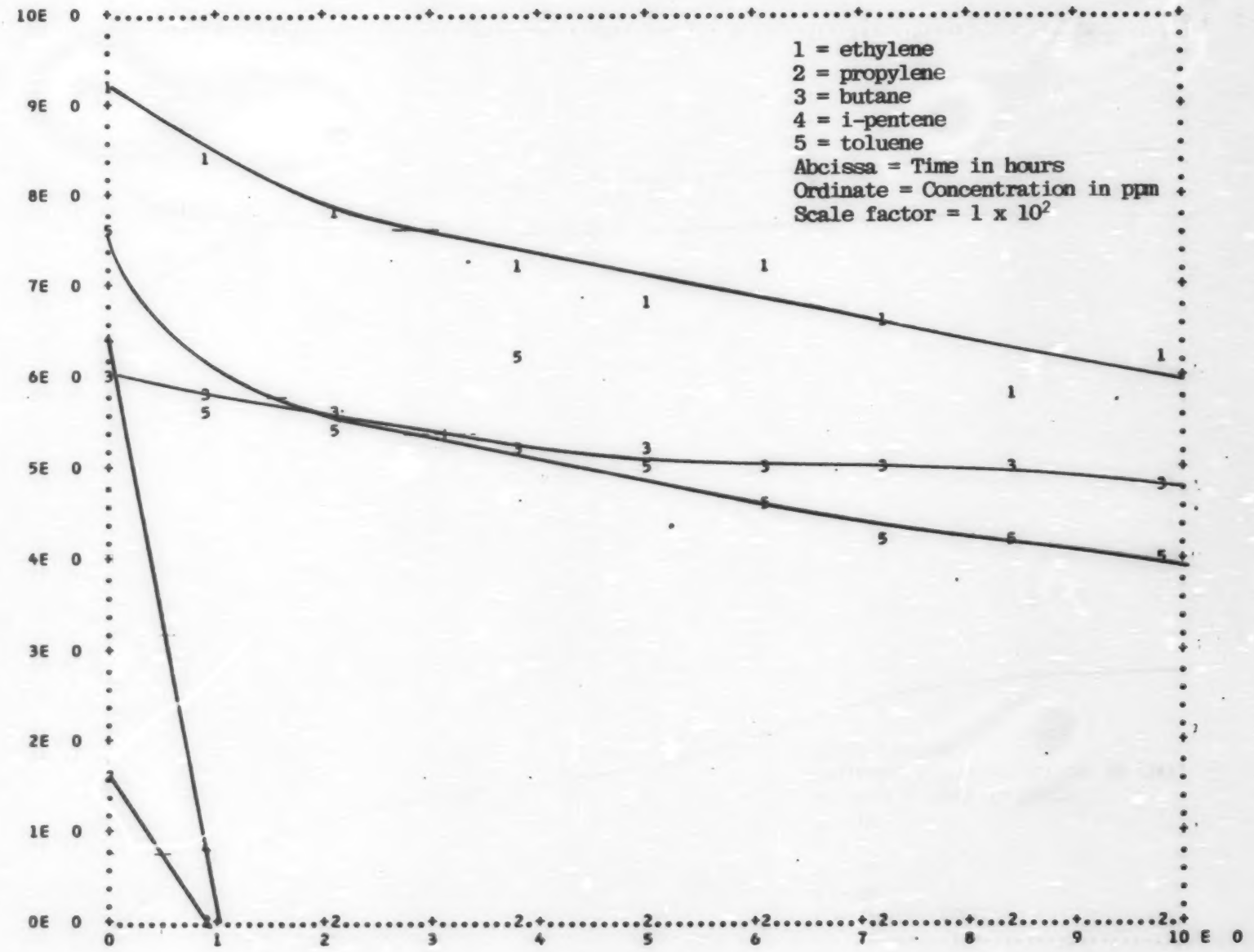
Final Formaldehyde by Chromatropic Acid = 0.04 ppm

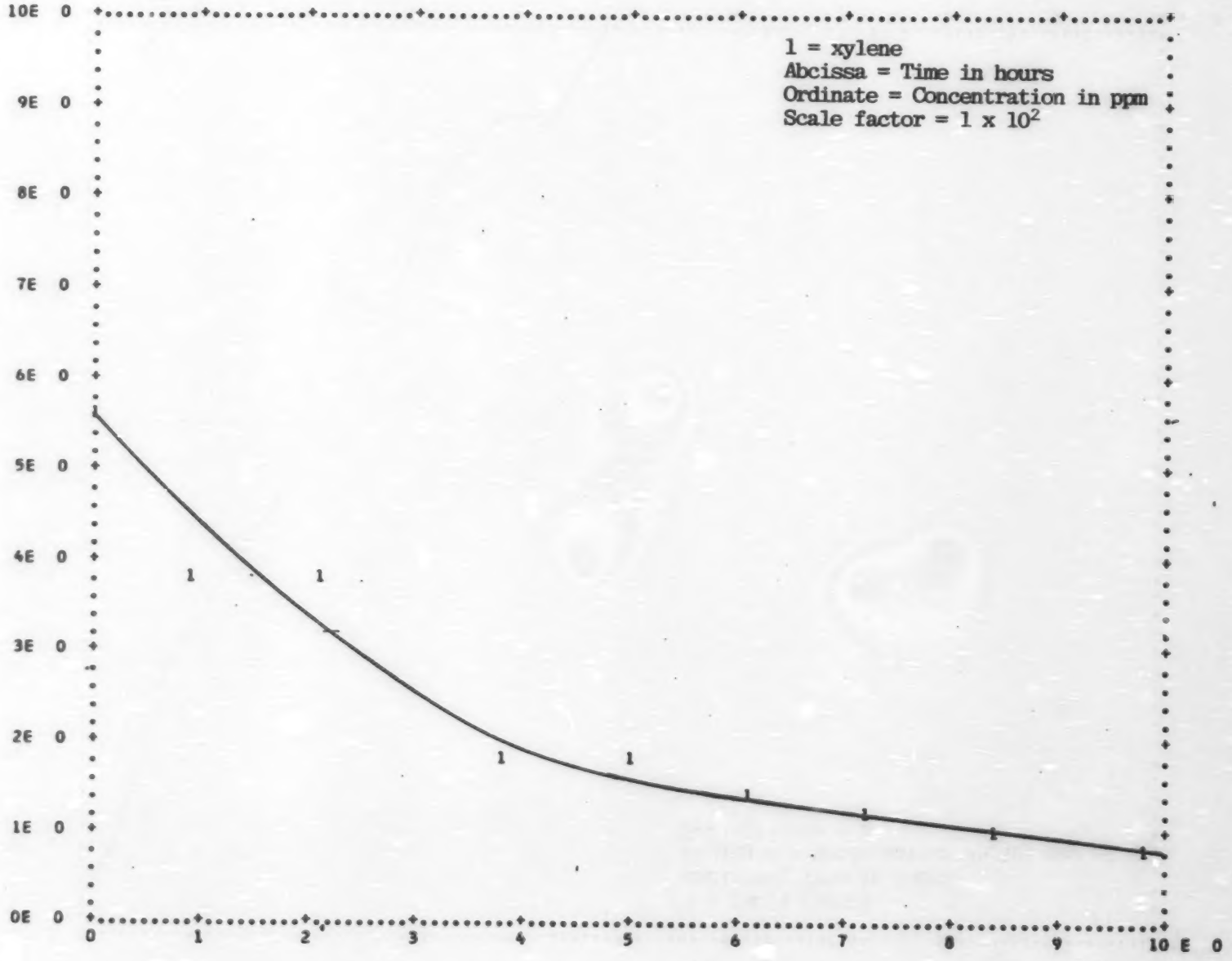
Maximum 1-hour O_3 Average = 0 ppm

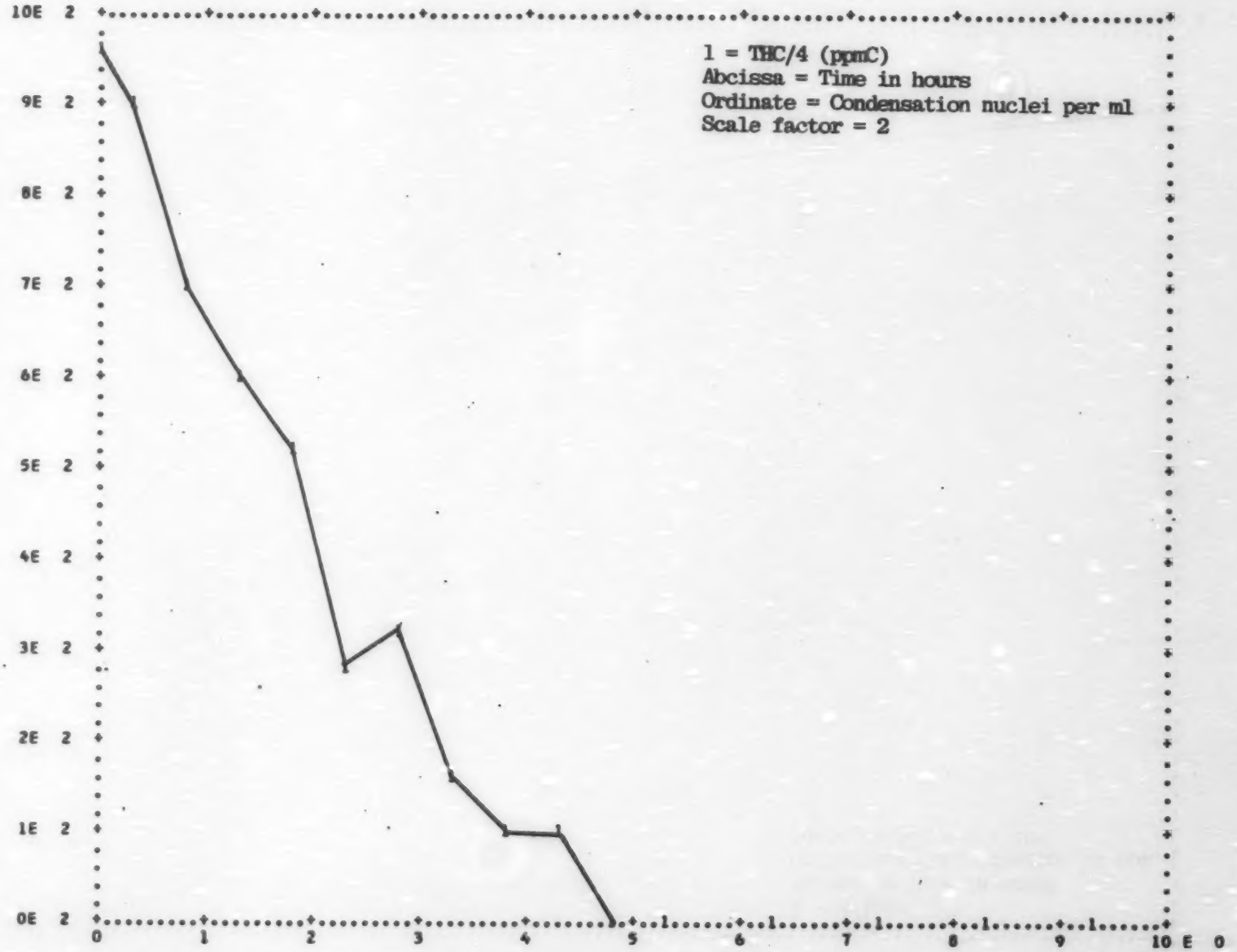
Maximum 1-hour NO_2 Average = 0.225

Average Hydrocarbon Disappearance Rates:
(1) ethylene = 0.0057
(2) propylene = 0.0160
(3) butane = 0.0019
(4) i-pentene = 0.0320
(5) toluene = 0.0121
(6) xylene = 0.0111


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale Factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0
1
2
3
4
5
6
7
8
9
10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 2
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0 1 2 3 4 5 6 7 8 9 10 E 0

RUN NO. 43: 4 ppm XL-263, 1 ppm NO_x, 0.3 ppm NO_2, DYNAMIC
September 23, 1975

Average Temperature = 33.31 ± 0.24 °C

Average Dilution Rate = $0.960 \times 10^{-1} \pm 0.132 \times 10^{-2}$ hr^{-1} chamber volumes

NO_2 Photolysis Rate Constant = Cannot calculate.
No intersection of NO and O_3 curves.

NO_2 Formation Rate = 0.22 ppm hr^{-1} (used time at maximum NO_2).

NO_2 Dose = 2.505 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0.02 ppm hr^{-1}

Average Rate of O_3 Formation = 0.01 ppm hr^{-1}

O_3 Dose = 0.238 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.42 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.68 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0.01 ppm

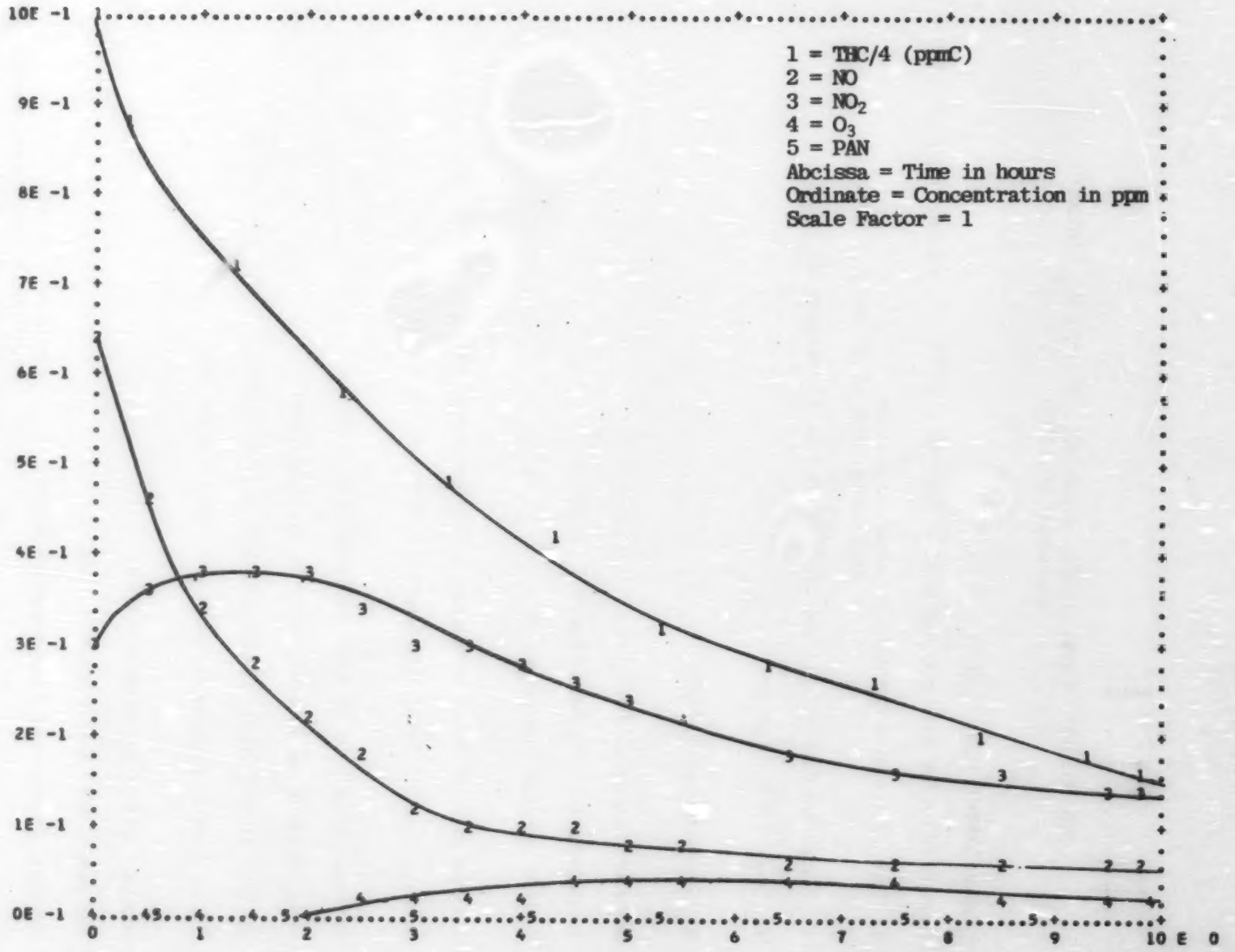
Initial Formaldehyde by Chromatropic Acid = 0 ppm

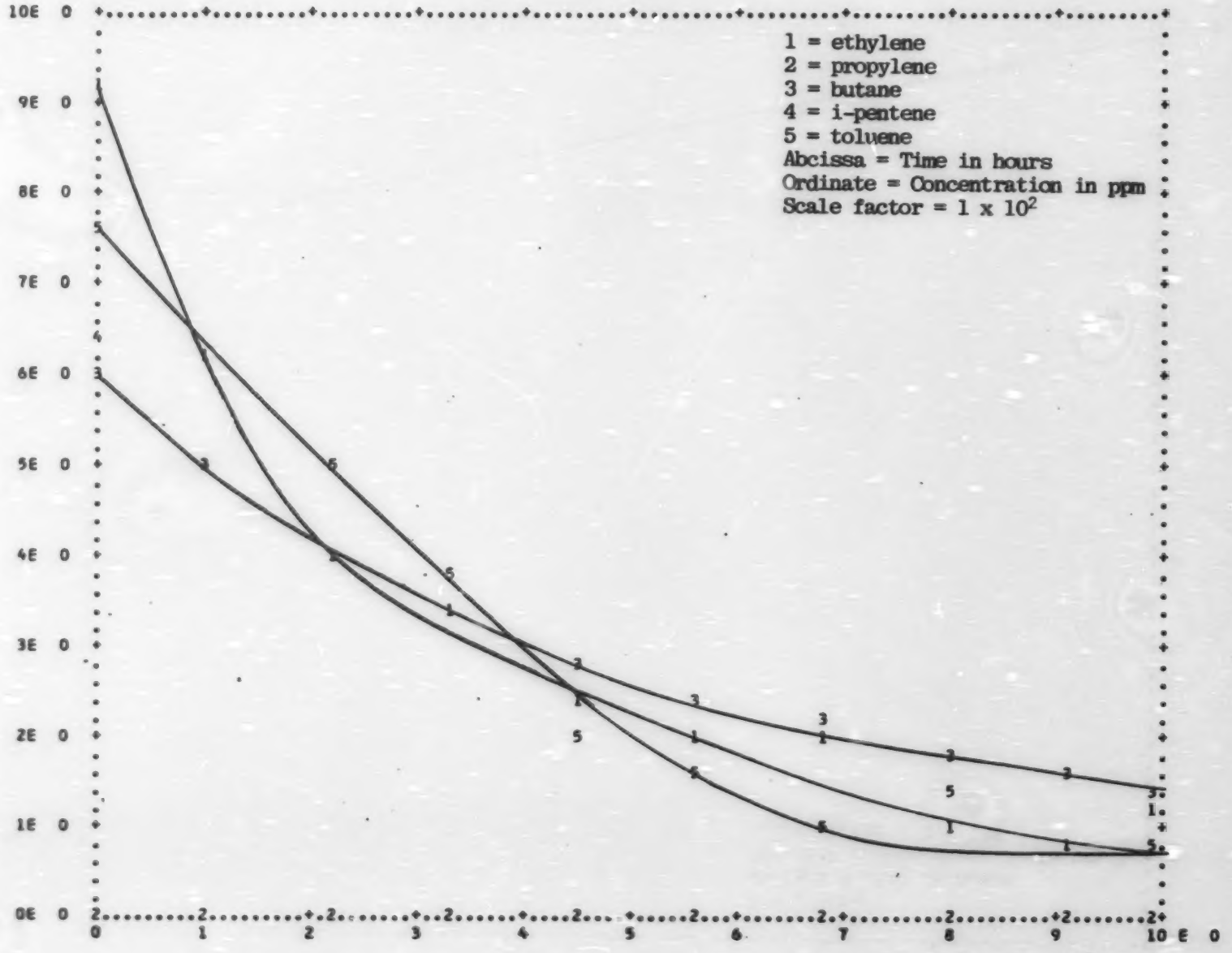
Final Formaldehyde by Chromatropic Acid = 0.04 ppm

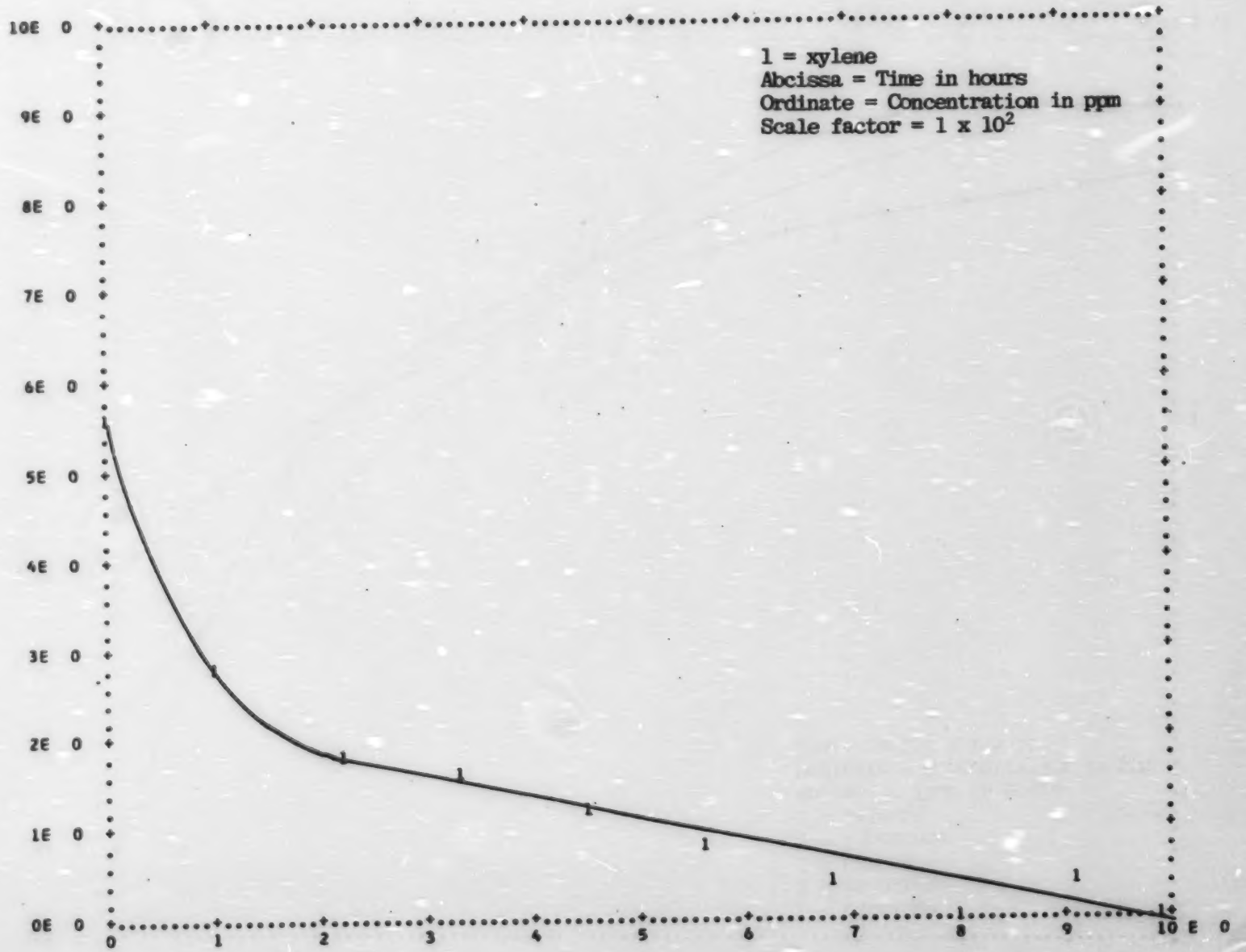
Maximum 1-hour O_3 Average = 0.05

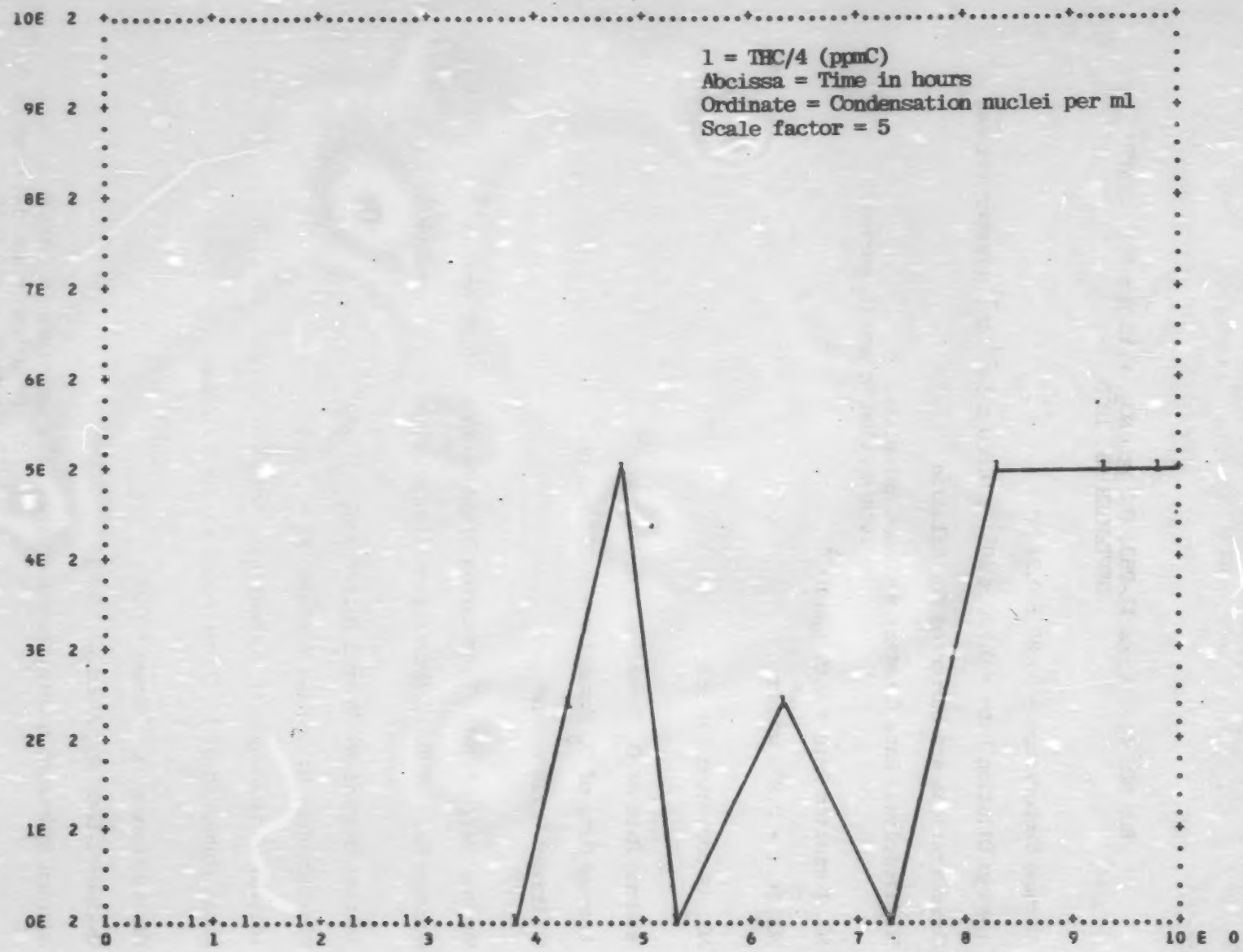
Maximum 1-hour NO_2 Average = 0.38

Average Hydrocarbon Disappearance Rates:
(1) ethylene = 0.0250
(2) propylene = none shown on GC
(3) butane = 0.0079
(4) i-pentene = only first reading shown on GC
(5) toluene = 0.0117
(6) xylene = 0.0280


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale Factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 5
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0 1 2 3 4 5 6 7 8 9 10 E 0

RUN NO. 44: 4 ppm XL-263, 0.5 ppm NO_x, 0.15 ppm NO_2, STATIC
SEPTEMBER 25, 1975

Average Temperature = 33.20 ± 0.24 °C

Average Dilution Rate = $0.120 \times 10^{-1} \pm 0.869 \times 10^{-3}$ hr^{-1} chamber volumes

Concentrations are corrected for dilution

NO_2 Photolysis Rate Constant = Cannot calculate.
No intersection No and O_3 curves.

NO_2 Formation Rate = 0.07 ppm hr^{-1}

NO_2 Dose = 2.239 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0.05 ppm hr^{-1}

Average Rate of O_3 Formation = 0.002 ppm hr^{-1}

O_3 Dose = 0.119 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.10 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.26 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0 ppm

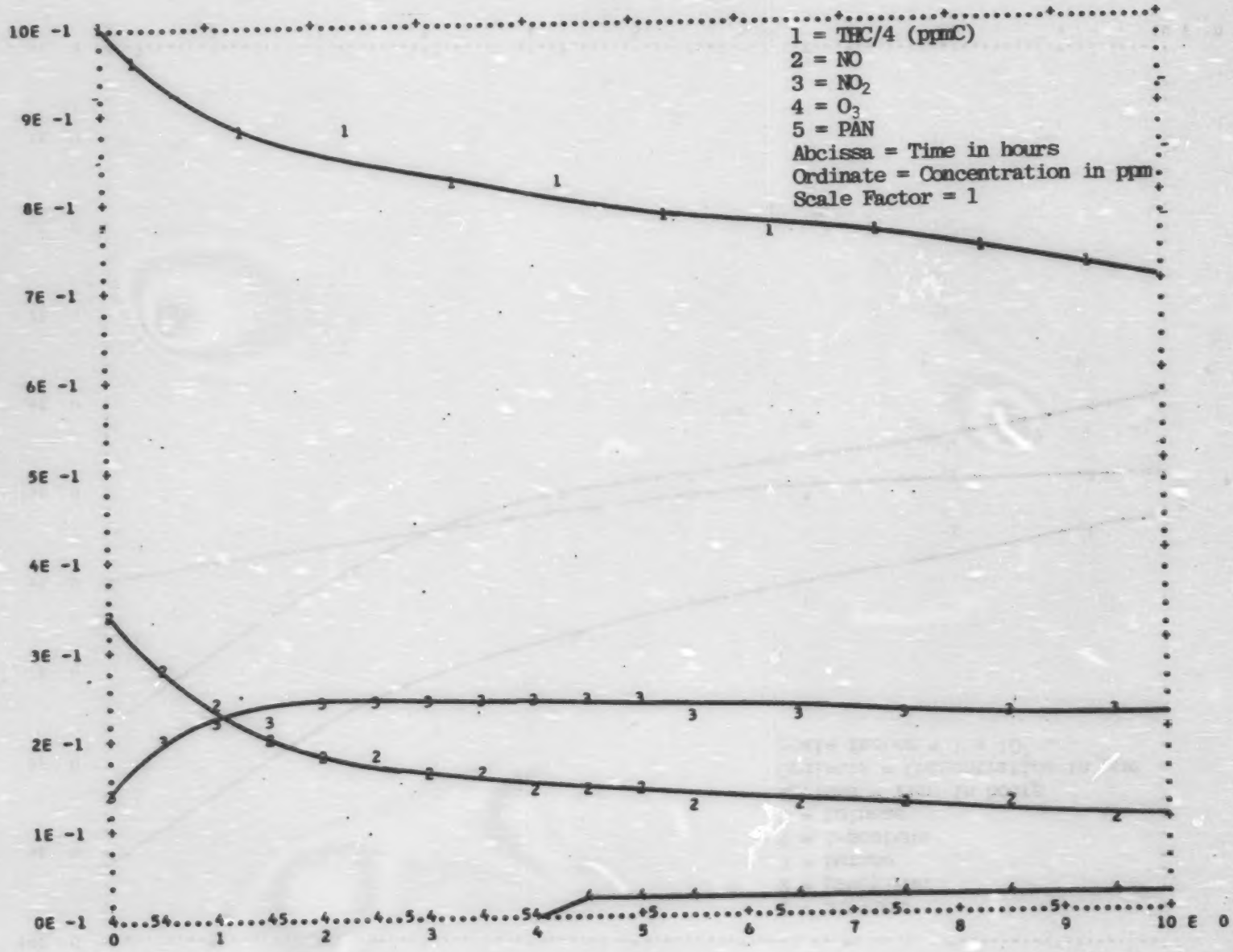
Initial Formaldehyde by Chromatropic Acid = 0 ppm

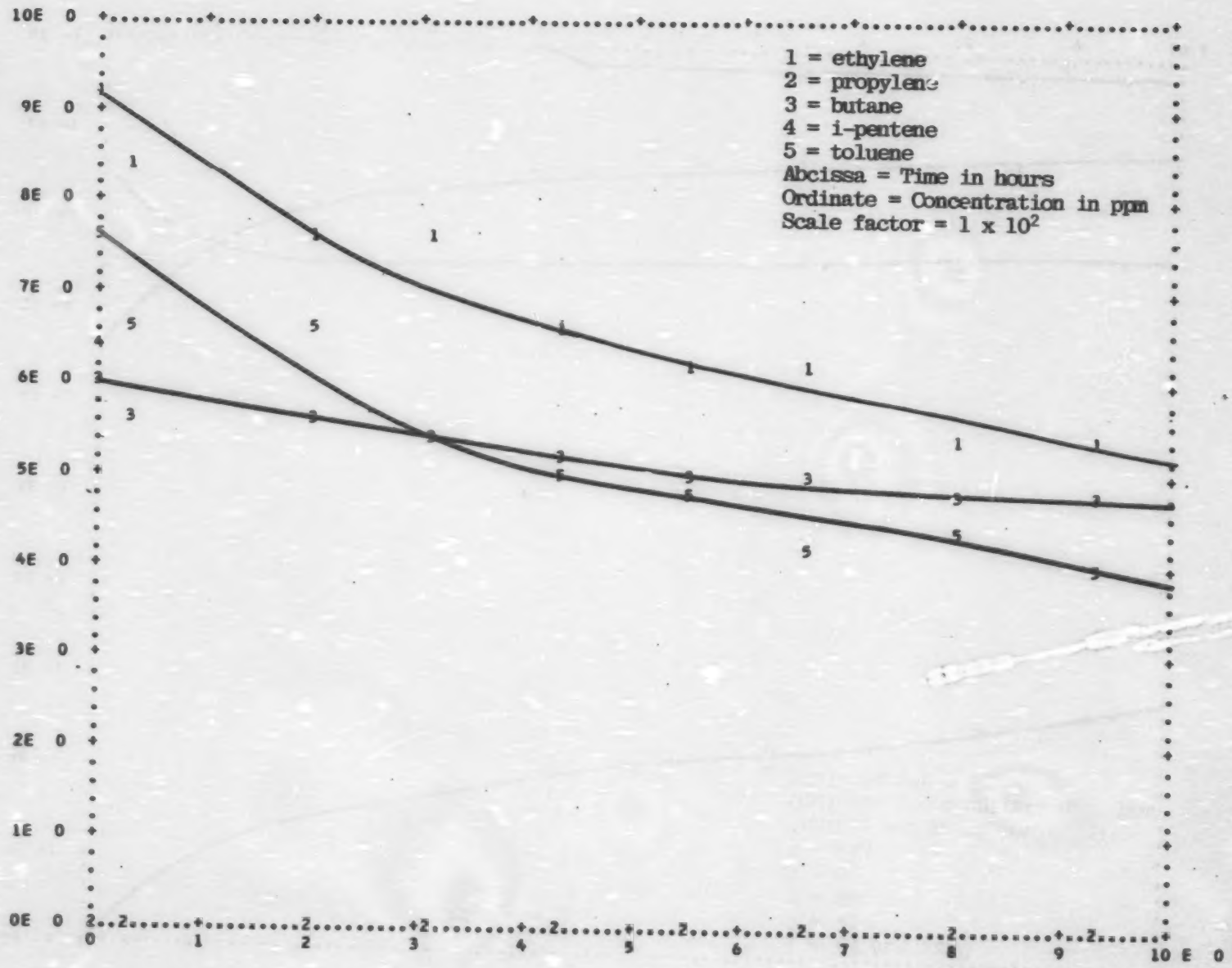
Final Formaldehyde by Chromatropic Acid = 0.07 ppm

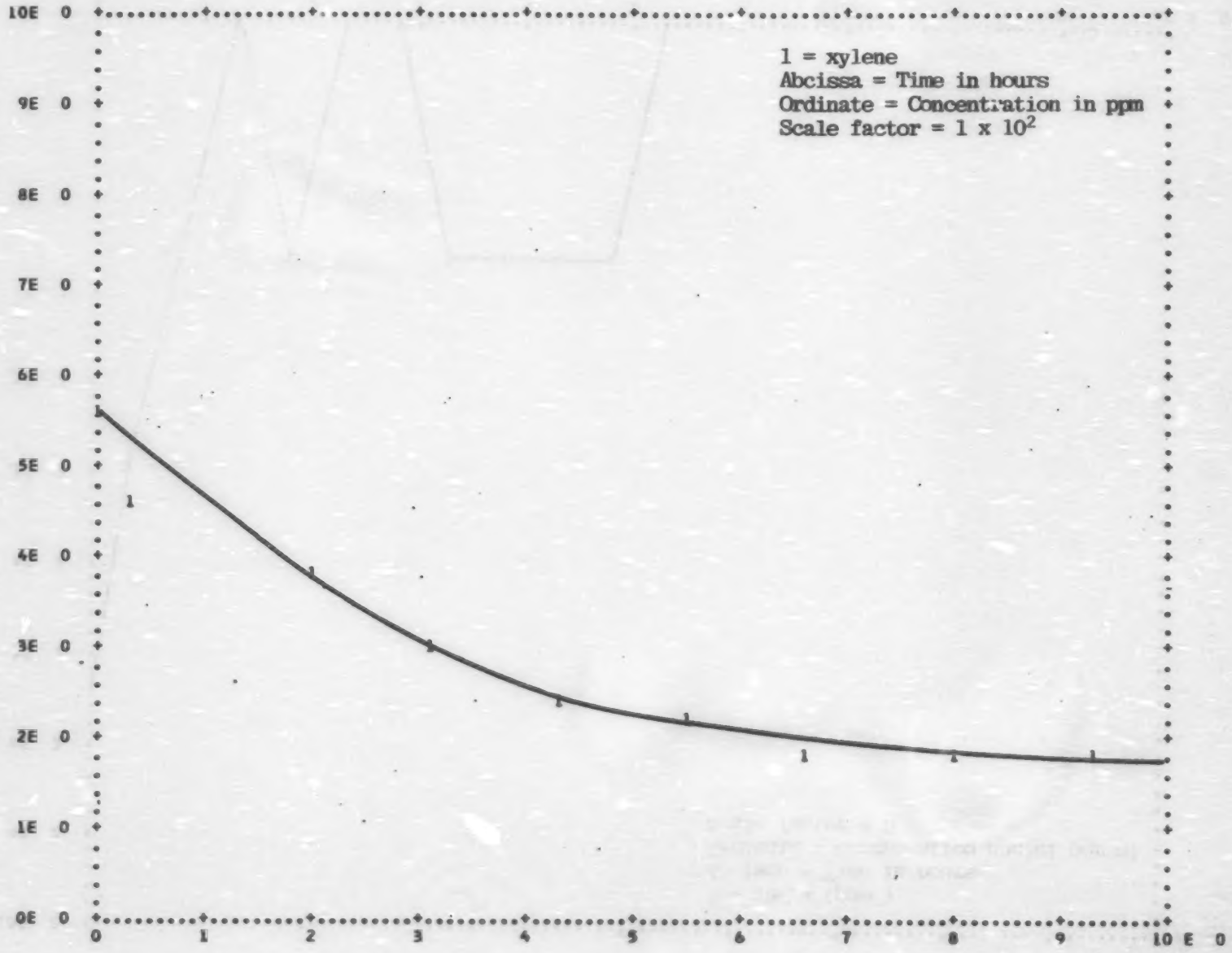
Maximum 1-hour O_3 Average = 0.02

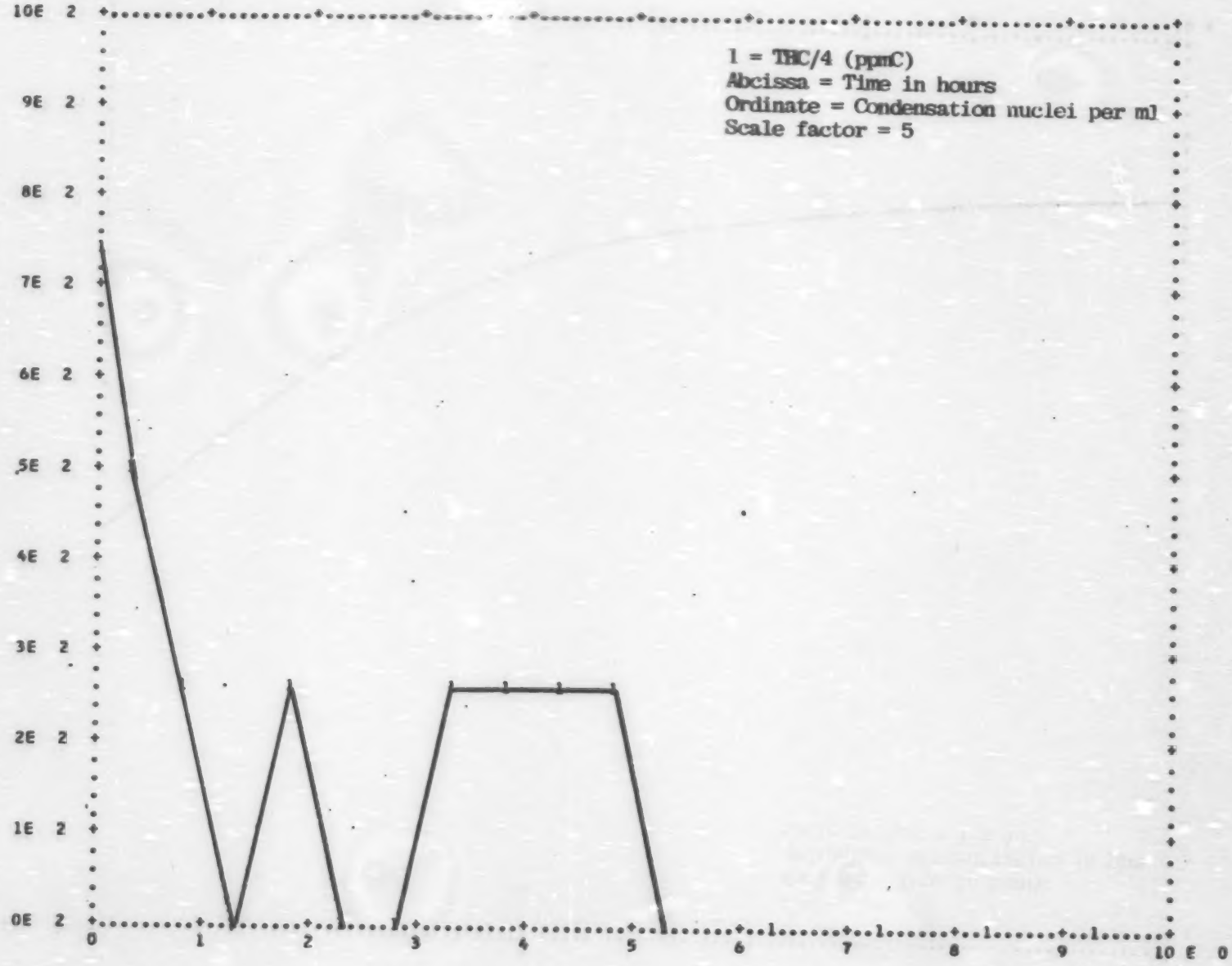
Maximum 1-hour NO_2 Average = 0.25

Average Hydrocarbon Disappearance Rate:
(1) ethylene = 0.0078
(2) propylene = not detected by GC
(3) butane = 0.0046
(4) i-pentene = GC showed only initial point
(5) toluene = 0.0074
(6) xylene = 0.0092


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale Factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0
1
2
3
4
5
6
7
8
9
10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 5
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0 1 2 3 4 5 6 7 8 9 10 E 0

RUN NO. 45: 4 ppm XL-263, 1 ppm NO_x, 0.3 ppm NO_2, DILUTION
SEPTEMBER 29, 1975

Average Temperature = 33.15 ± 0.23 °C

Average Dilution Rate = $0.556 \times 10^{-1} \pm 0.136 \times 10^{-1}$ hr^{-1} chamber volumes

NO_2 Photolysis Rate Constant = Cannot calculate.
No intersection of NO and O_3 curves.

NO_2 Formation Rate = 0.18 ppm hr^{-1}

NO_2 Dose = 2.892 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0 ppm hr^{-1}

Average Rate of O_3 Formation = 0 ppm hr^{-1}

O_3 Dose = 0.017 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.27 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.24 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Bufffered KI = 0.04 ppm

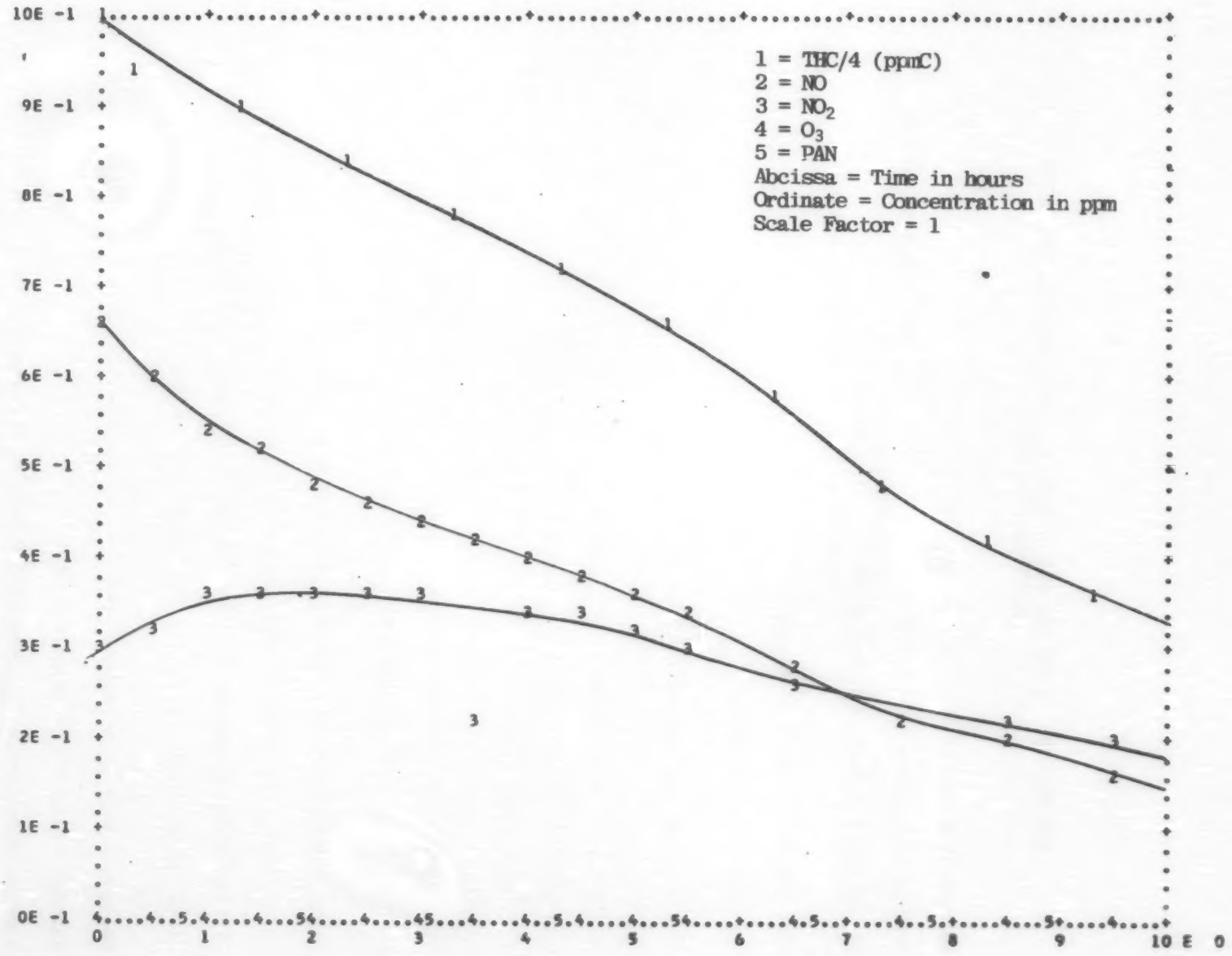
Initial Formaldehyde by Chromatropic Acid = 0 ppm

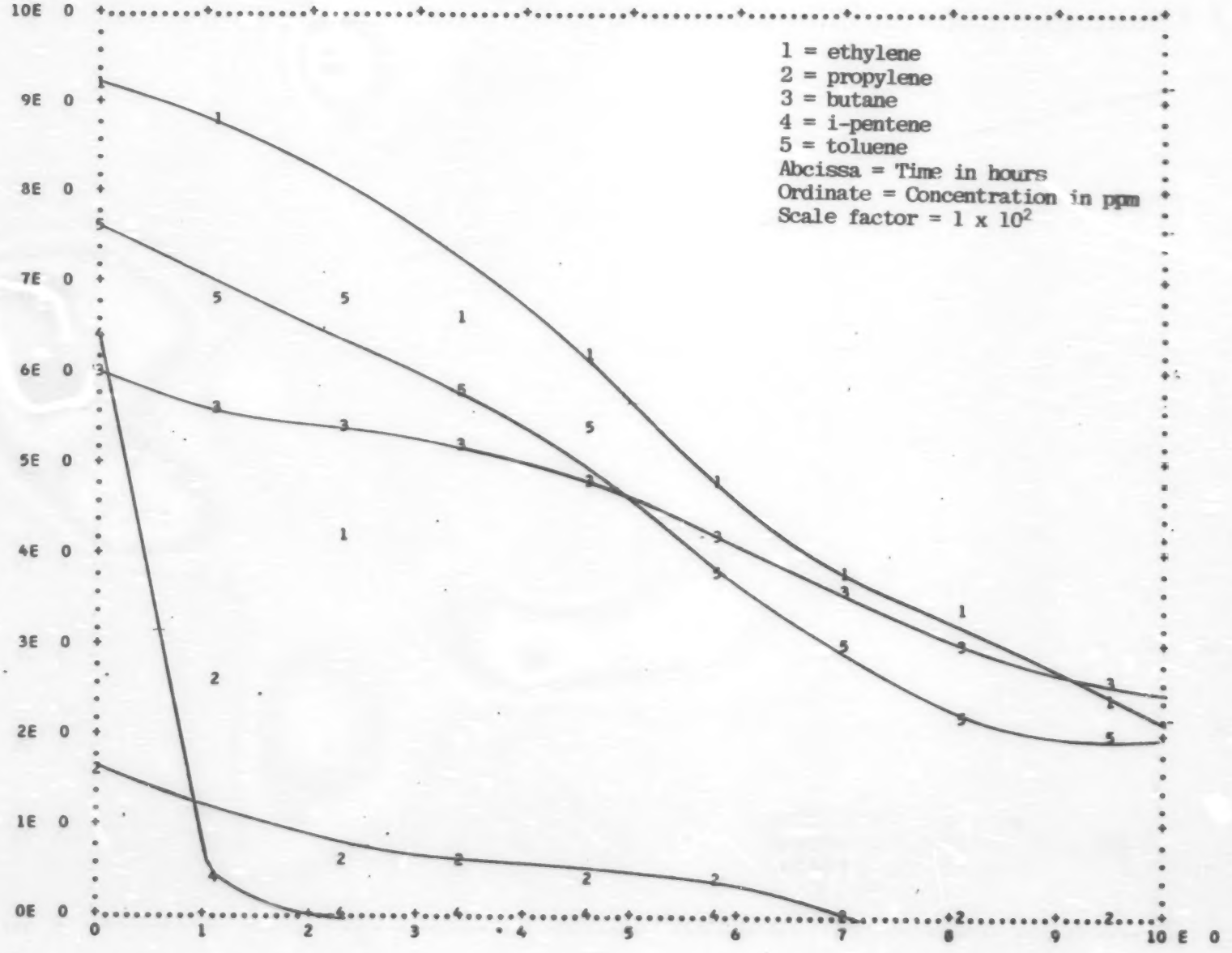
Final Formaldehyde by Chromatropic Acid = 0.04 ppm

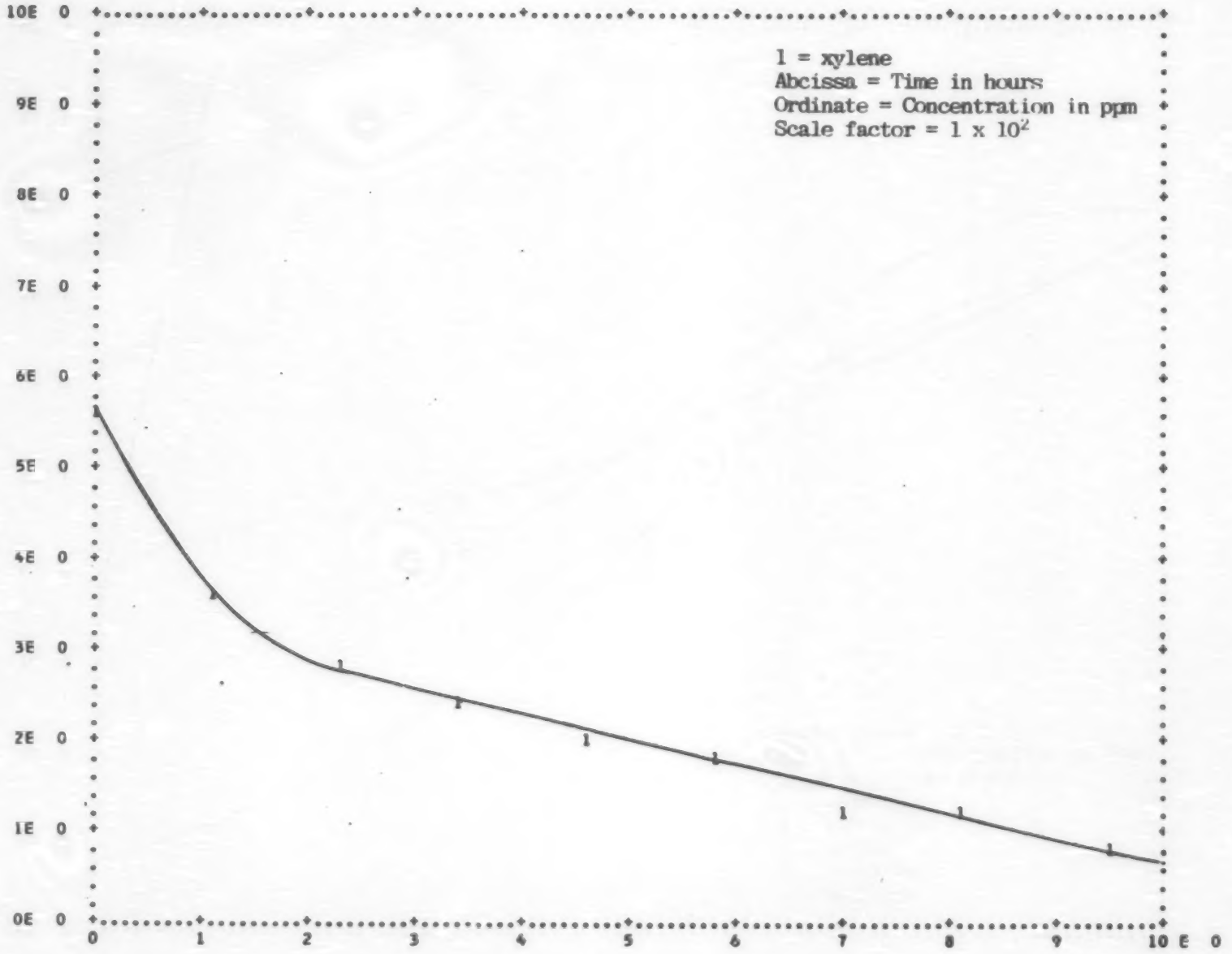
Maximum 1-hour O_3 Average = .001

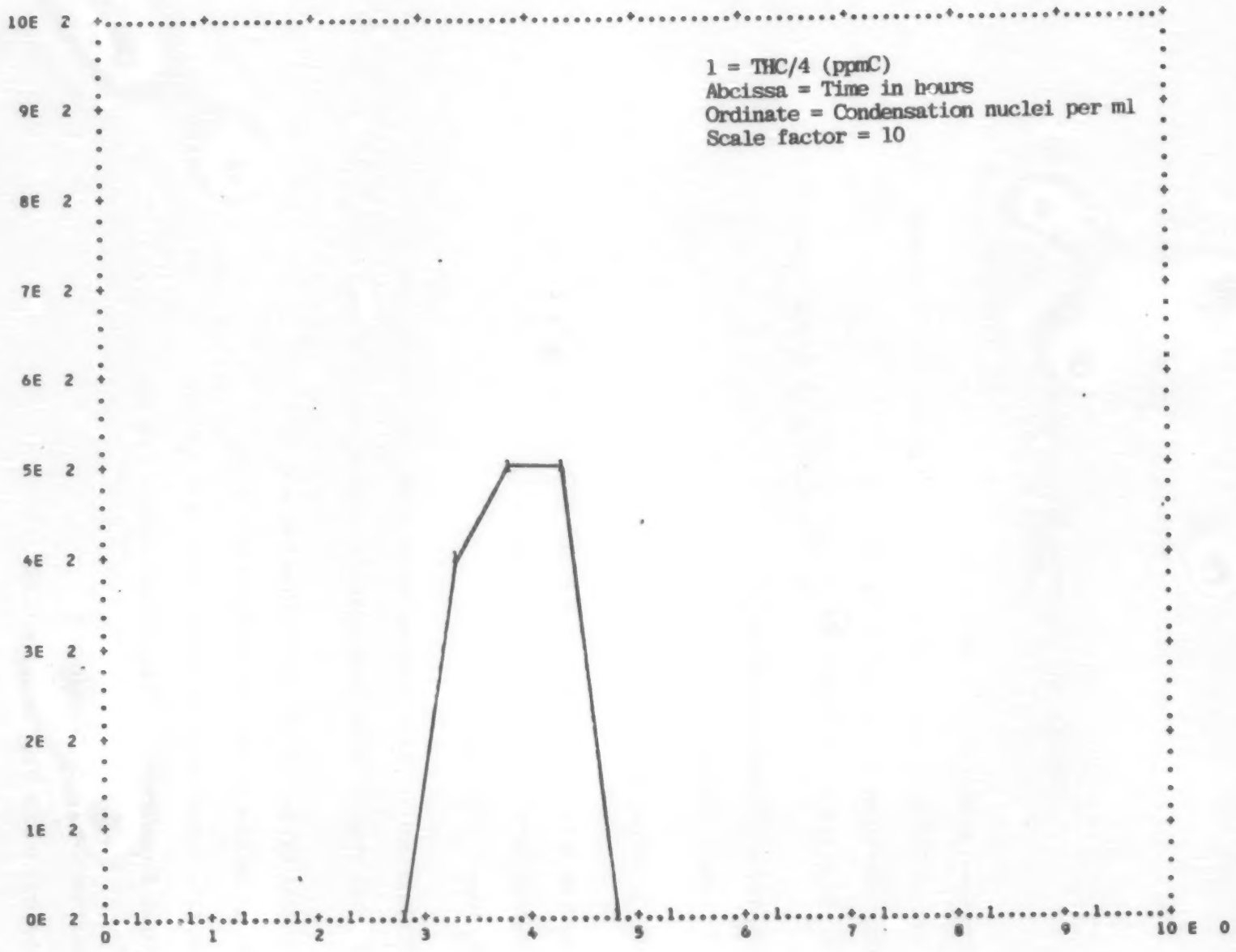
Maximum 1-hour NO_2 Average = 0.36

Average Hydrocarbon Disappearance Rates:
(1) ethylene = 0.0068
(2) propylene = 0.0032
(3) butane = 0.0029
(4) i-pentene = 0.0533
(5) toluene = 0.0059
(6) xylene = 0.0157


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale Factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0
1
2
3
4
5
6
7
8
9
10 E 0


10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 10
0
1
2
3
4
5
6
7
8
9
10 E 0

RUN NO. 46: 4 ppm XL-263, 1 ppm NO_x, 0.3 ppm NO_2, STATIC
OCTOBER 1, 1975

Average Temperature = 33.18 ± 0.23 °C

Average Dilution Rate = $0.118 \times 10^{-1} \pm 0.782 \times 10^{-3}$ hr^{-1} chamber volumes

Concentrations are corrected for dilution

NO_2 Photolysis Rate Constant = Cannot calculate.
No intersection of NO and O_3 curves.

NO_2 Formation Rate = 0.64 ppm hr^{-1}

NO_2 Dose = 3.538 ppm hr

NO_2 is corrected for PAN

Maximum Rate of O_3 Formation = 0 ppm hr^{-1}

Average Rate of O_3 Formation = 0 ppm hr^{-1}

O_3 Dose = 0.005 ppm hr

Maximum Rate of Total Hydrocarbon Disappearance = 0.10 ppmC hr^{-1}

Average Rate of Total Hydrocarbon Disappearance = 0.15 ppmC hr^{-1}

Initial Oxidant by Neutral Buffered KI = 0 ppm

Final Oxidant by Neutral Buffered KI = 0 ppm

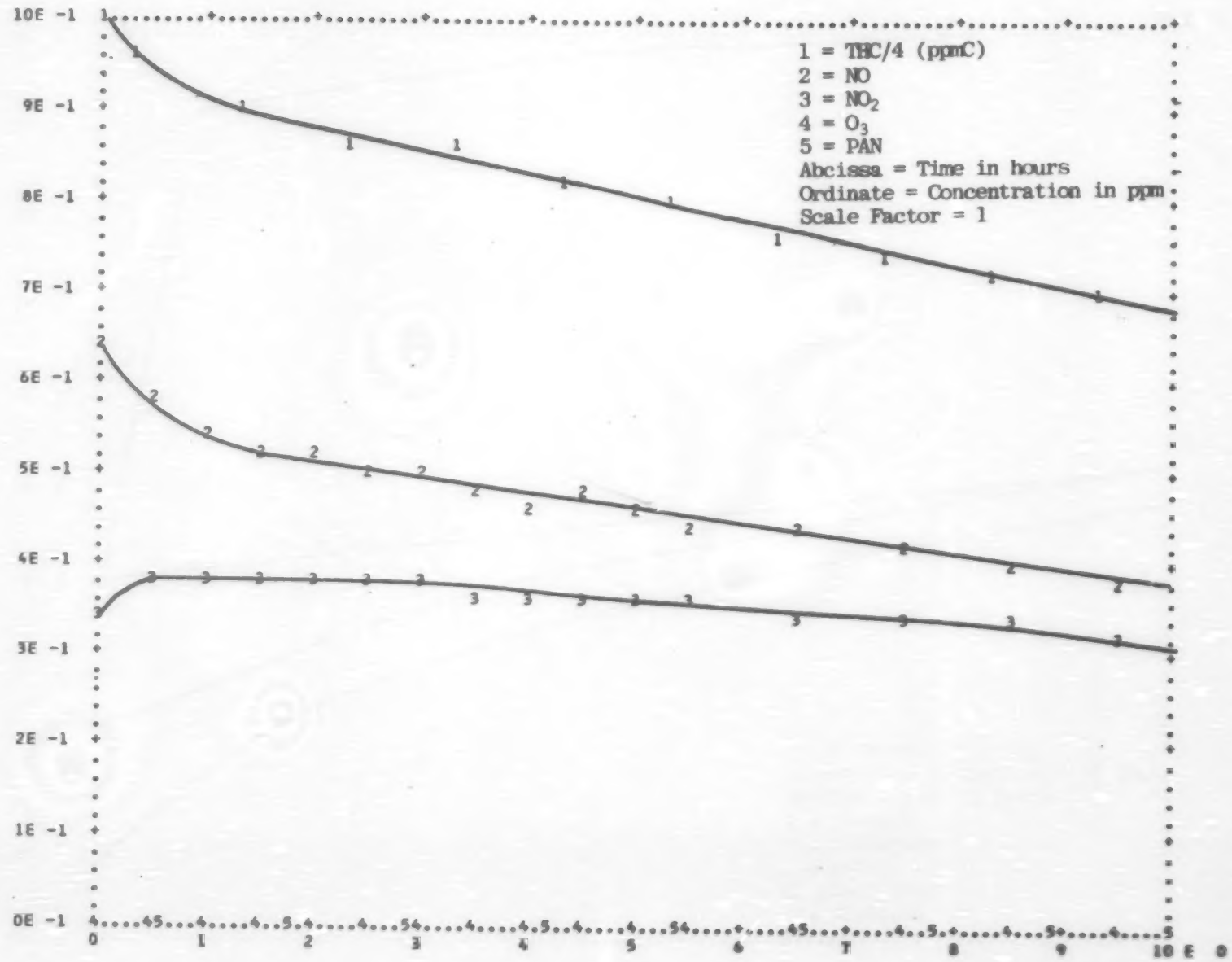
Initial Formaldehyde by Chromatropic Acid = 0 ppm

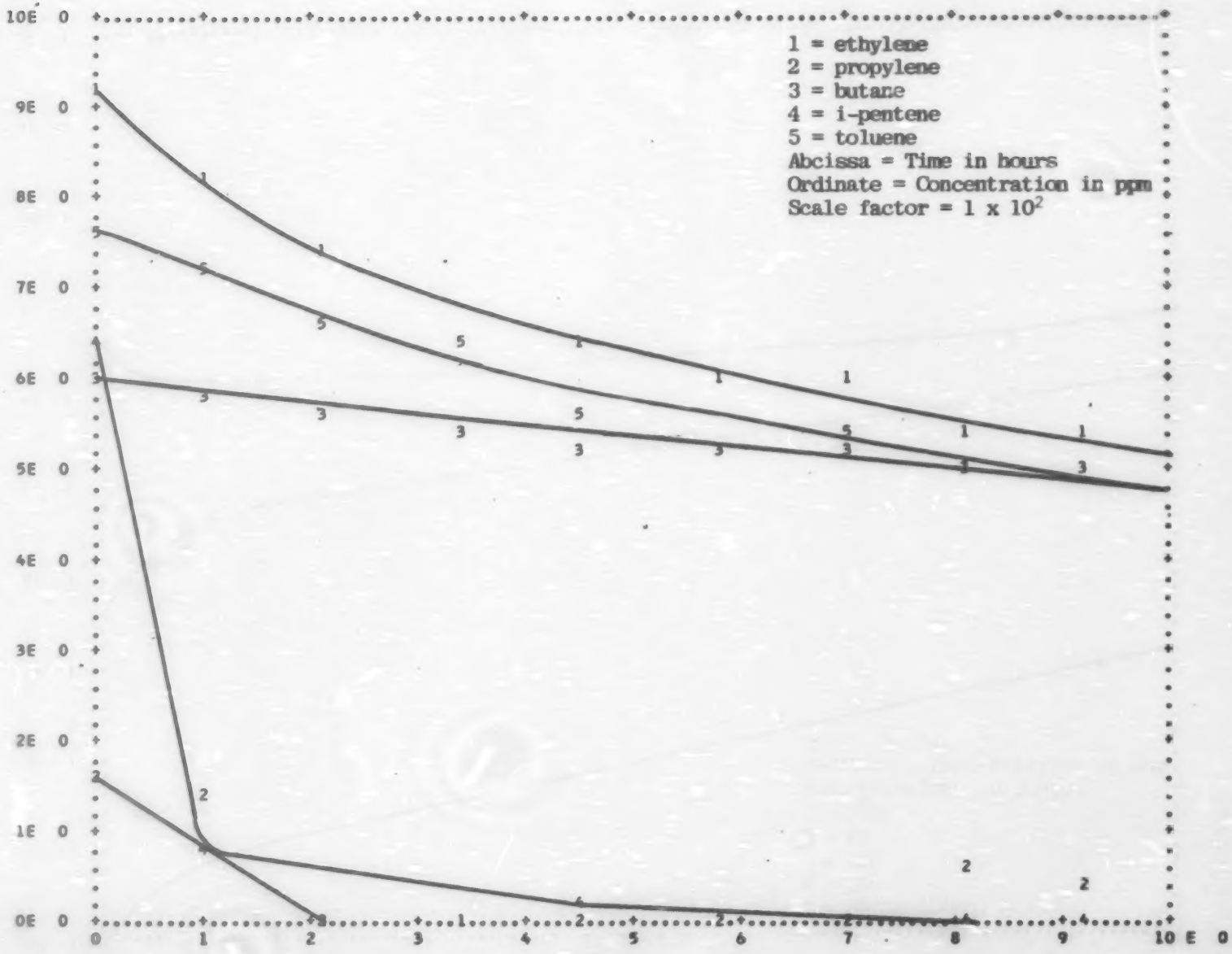
final Formaldehyde by Chromatropic Acid = 0.06 ppm

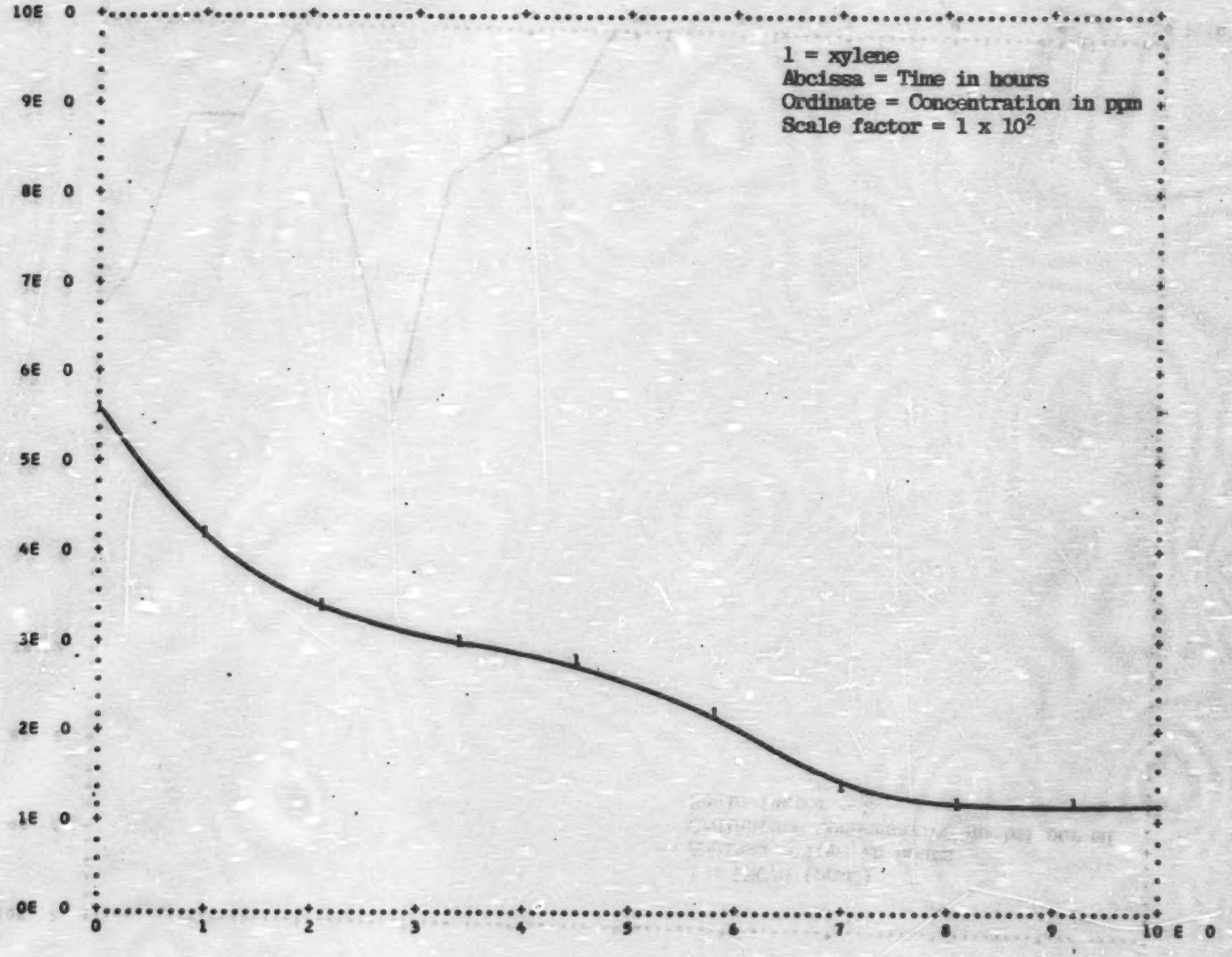
Maximum 1-hour O_3 Average = 0

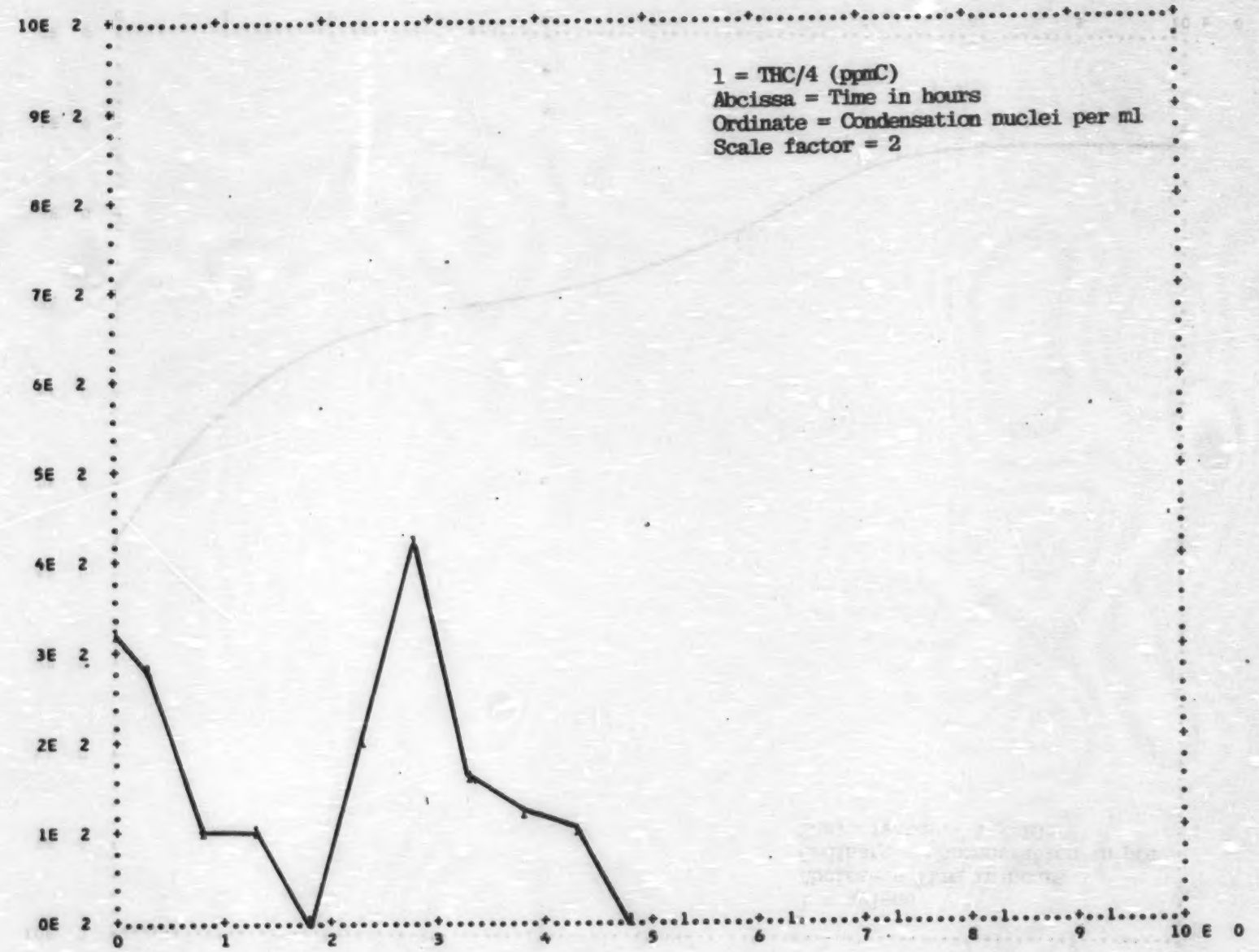
Maximum 1-hour NO_2 Average = 0.385

Average Hydrocarbon Disappearance Rates:
(1) ethylene = 0.0086
(2) propylene = 0.0072
(3) toluene = 0.0014
(4) i-pentene = 0.0533
(5) toluene = 0.0037
(6) xylene = 0.0127


1 = THC/4 (ppmC)
2 = NO
3 = NO2
4 = O3
5 = PAN
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale Factor = 1
10E -1
9E -1
8E -1
7E -1
6E -1
5E -1
4E -1
3E -1
2E -1
1E -1
0E -1
0
1
2
3
4
5
6
7
8
9
10 E 0


1 = ethylene
2 = propylene
3 = butane
4 = i-pentene
5 = toluene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0 1 2 3 4 5 6 7 8 9 10 E 0


1 = xylene
Abcissa = Time in hours
Ordinate = Concentration in ppm
Scale factor = 1 x 10²
10E 0
9E 0
8E 0
7E 0
6E 0
5E 0
4E 0
3E 0
2E 0
1E 0
0E 0
0
1
2
3
4
5
6
7
8
9
10 E 0


1 = THC/4 (ppmC)
Abcissa = Time in hours
Ordinate = Condensation nuclei per ml
Scale factor = 2
10E 2
9E 2
8E 2
7E 2
6E 2
5E 2
4E 2
3E 2
2E 2
1E 2
0E 2
0
1
2
3
4
5
6
7
8
9
10 E 0

APPENDIX C

ANALYSIS OF VARIANCE TABLES

PARAMETER: MAXIMUM 1-HOUR AVERAGE O_3

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	8.335×10^{-8}	1	8.335×10^{-8}	$HC/NO_x = 4$	5.299×10^{-2}
Mode of Operation	6.267×10^{-3}	2	3.133×10^{-3}	$HC/NO_x = 8$	5.283×10^{-2}
Interaction	6.250×10^{-3}	2	3.125×10^{-3}	Static	4.024×10^{-2}
Error	1.669×10^{-2}	6	2.782×10^{-3}	Dynamic	3.350×10^{-2}
Total	2.921×10^{-2}	11		Dilution	8.499×10^{-2}
Grand Mean	5.291×10^{-2}				
Error Std. Deviation	5.275×10^{-2}				

PARAMETER: O_3 DOSE

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	9.020×10^{-3}	1	9.020×10^{-3}	$HC/NO_x = 4$	2.816×10^{-1}
Mode of Operation	3.072×10^{-1}	2	1.536×10^{-3}	$HC/NO_x = 8$	3.365×10^{-1}
Interaction	1.888×10^{-1}	2	9.443×10^{-2}	Static	1.732×10^{-1}
Error	6.946×10^{-1}	6	1.157×10^{-1}	Dynamic	2.202×10^{-1}
Total	1.199×10^{0}	11		Dilution	5.337×10^{-1}
Grand Mean	3.090×10^{-1}				
Error Std. Deviation	3.402×10^{-1}				

PARAMETER: NO_2 DOSE

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	2.980×10^{0}	1	2.980×10^{0}	$HC/NO_x = 4$	3.115×10^{0}
Mode of Operation	7.568×10^{-1}	2	3.784×10^{-1}	$HC/NO_x = 8$	2.118×10^{0}
Interaction	1.302×10^{0}	2	6.514×10^{-1}	Static	2.965×10^{0}
Error	2.821×10^{-1}	6	4.703×10^{-2}	Dynamic	2.502×10^{0}
Total	5.321×10^{0}	11		Dilution	2.384×10^{0}
Grand Mean	2.616×10^{0}				
Error Std. Deviation	2.168×10^{-1}				

PARAMETER: NO_2, TIME TO MAXIMUM

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	1.540×10^0	1	1.540×10^0	$HC/NO_x = 4$	1.000×10^0
Mode of Operation	4.531×10^0	2	2.265×10^0	$HC/NO_x = 8$	1.716×10^0
Interaction	7.181×10^0	2	3.590×10^0	Static	2.200×10^0
Error	9.950×10^{-1}	6	1.658×10^{-1}	Dynamic	1.125×10^0
Total	1.424×10^1	11		Dilution	7.500×10^{-1}
Grand Mean	1.358×10^0				
Error Std. Deviation	4.072×10^{-1}				

PARAMETER: O_3, TIME TO MAXIMUM

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	3.307×10^0	1	3.307×10^0	$HC/NO_x = 4$	6.966×10^0
Mode of Operation	4.853×10^1	2	2.426×10^1	$HC/NO_x = 8$	5.916×10^0
Interaction	9.214×10^0	2	4.607×10^0	Static	8.875×10^0
Error	9.095×10^0	6	1.515×10^0	Dynamic	6.500×10^0
Total	7.014×10^1	11		Dilution	3.950×10^0
Grand Mean	6.441×10^0				
Error Std. Deviation	1.231×10^0				

PARAMETER: MAXIMUM 1-HOUR AVERAGE NO_2

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	7.760×10^{-2}	1	7.760×10^{-2}	$HC/NO_x = 4$	4.050×10^{-1}
Mode of Operation	2.804×10^{-3}	2	1.402×10^{-3}	$HC/NO_x = 8$	2.441×10^{-1}
Interaction	1.654×10^{-3}	2	8.270×10^{-4}	Static	3.037×10^{-1}
Error	1.361×10^{-2}	6	2.268×10^{-3}	Dynamic	3.400×10^{-1}
Total	9.567×10^{-2}	11		Dilution	3.300×10^{-1}
Grand Mean	3.245×10^{-1}				
Error Std. Deviation	4.763×10^{-2}				

PARAMETER: FINAL FORMALDEHYDE

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	4.033×10^{-3}	1	4.033×10^{-3}	$HC/NO_x = 4$	8.666×10^{-2}
Mode of Operation	9.516×10^{-3}	2	4.758×10^{-3}	$HC/NO_x = 8$	5.000×10^{-2}
Interaction	7.016×10^{-3}	2	3.508×10^{-3}	Static	1.074×10^{-1}
Error	2.139×10^{-2}	6	3.566×10^{-3}	Dynamic	5.500×10^{-2}
Total	4.196×10^{-2}	11		Dilution	4.250×10^{-2}
Grand Mean	6.833×10^{-2}				
Error Std. Deviation	5.972×10^{-2}				

PARAMETER: AVERAGE TOTAL HYDROCARBON DISAPPERANCE RATE

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	1.840×10^{-2}	1	1.840×10^{-2}	$HC/NO_x = 4$	4.133×10^{-1}
Mode of Operation	1.035×10^{0}	2	5.175×10^{-1}	$HC/NO_x = 8$	4.916×10^{-1}
Interaction	1.421×10^{-2}	2	7.108×10^{-3}	Static	2.299×10^{-1}
Error	9.265×10^{-2}	6	1.544×10^{-2}	Dynamic	2.600×10^{-1}
Total	1.160×10^{0}	11		Dilution	8.675×10^{-1}
Grand Mean	4.524×10^{-1}				
Error Std. Deviation	1.242×10^{-1}				

PARAMETER: PAN, MAXIMUM

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	7.499×10^{-7}	1	7.499×10^{-7}	$HC/NO_x = 4$	1.999×10^{-3}
Mode of Operation	3.049×10^{-5}	2	1.524×10^{-5}	$HC/NO_x = 8$	1.499×10^{-3}
Interaction	6.499×10^{-6}	2	3.249×10^{-6}	Static	5.000×10^{-4}
Error	3.850×10^{-5}	6	6.416×10^{-6}	Dynamic	7.500×10^{-4}
Total	7.625×10^{-5}	11		Dilution	4.000×10^{-3}
Grand Mean	1.749×10^{-3}				
Error Std. Deviation	2.533×10^{-3}				

PARAMETER: FINAL OXIDANT

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Factor Means	
HC/NO_x	4.083×10^{-4}	1	4.083×10^{-4}	$HC/NO_x = 4$	4.166×10^{-2}
Mode of Operation	1.016×10^{-3}	2	5.083×10^{-4}	$HC/NO_x = 8$	3.000×10^{-2}
Interaction	5.216×10^{-3}	2	2.608×10^{-3}	Static	3.500×10^{-2}
Error	1.504×10^{-2}	6	2.508×10^{-3}	Dynamic	4.749×10^{-2}
Total	2.169×10^{-2}	11		Dilution	2.500×10^{-2}
Grand Mean	3.583×10^{-2}				
Error Std. Deviation	5.008×10^{-2}				